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Land Disposal of Hazardous Wastes

Proceedings of the Fourth Annual Research Symposium

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The fourth SHWRD research symposium on land disposal of hazardous waste was held at the St. Anthony Hotel in San Antonio on March 6, 7, and 8, 1978. The purpose of the symposium was two-fold: (1) to provide a forum for a state-of-the-art review and discussion of ongoing and recently-completed research projects dealing with the management of hazardous wastes and (2) to bring together people concerned with hazardous waste management who can benefit from an exchange of ideas and information. These proceedings are a compilation of the papers presented by symposium speakers. They are arranged in the order of presentation. The five primary technical areas covered are

(1) Methods development and economic assessment,
(2) Identification of pollutant potential,
(3) Predicting trace element migration,
(4) Modification of disposal sites and waste streams, and
(5) Alternatives for land disposal.

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FOREWORD

The Environmental Protection Agency was created because of increasing public and governmental concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of the environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is the first necessary step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and the solid and hazardous waste pollutant discharges from municipal and community sources; to preserve and treat public drinking water supplies; and to minimize the adverse economic, social, health and aesthetic effects of pullution. This publication is one of the products of that research--a vital communications link between the researcher and the user community.

The proceedings present research aimed at minimizing the impact of direct land disposal of hazardous wastes and provide solutions to specific problems.

Francis T. Mayo
Director
Municipal Environmental
Research Laboratory

PREFACE

These proceedings are intended to disseminate up-to-date information on extramural research projects dealing with the disposal of solid and hazardous wastes. These projects are funded by the Solid and Hazardous Waste Research Division (SHWRD) of the U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory in Cincinnati, Ohio. Selected papers from work of other organizations were included in the symposium to identify closely-related work not included in the SHWRD program.

The papers in these proceedings are arranged as they were presented at the symposium. Each of the five sessions includes papers dealing with major areas of interest for those involved in hazardous waste management and research.

The papers are printed here basically as received from the symposium authors. They do not necessarily reflect the policies and opinions of the U.S. Environmental Protection Agency or Southwest Research Institute. Hopefully, these proceedings will prove useful and beneficial to the scientific community as a current reference on land disposal of hazardous wastes.

ABSTRACT

The fourth SHWRD research symposium on land disposal of hazardous waste was held at the St. Anthony Hotel in San Antonio on March 6, 7 and 8, 1978. The purpose of the symposium was two-fold: (1) to provide a forum for a state-of-the-art review and discussion of ongoing and recently-completed research projects dealing with the management of hazardous wastes and (2) to bring together people concerned with hazardous waste management who can benefit from an exchange of ideas and information. These proceedings are a compilation of the papers presented by symposium speakers. They are arranged in the order of presentation. The five primary technical areas covered are

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CURRENT RESEARCH ON LAND DISPOSAL OF HAZARDOUS WASTES

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ABSTRACT

The Solid and Hazardous Waste Research Division (SHWRD), Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, in Cincinnati, Ohio, has responsibility for research in the areas of solid and hazardous waste management, including both disposal and processing. To fulfill this responsibility, the SHWRD is developing concepts and technology for new and improved systems of solid and hazardous waste management; is documenting the environmental effects of various waste processing and disposal practices; and is collecting data necessary to support implementation of processing and disposal guidelines mandated by the recently enacted Resource Conservation and Recovery Act (RCRA). This paper will present an overview of the land disposal aspects of the SHWRD hazardous waste program plan and will report the current status of work in the following categorical areas:

1. Waste Characterization/Decomposition
2. Pollutant Transport
3. Pollutant Control
4. Pollutant Treatment
5. Co-Disposal
6. Remedial Action
7. Landfill Alternatives/Land Cultivation
8. Economic/Environmental Impact

INTRODUCTION

The waste residual disposal research strategy, encompassing state-of-the-art documents, laboratory analysis, bench and pilot studies, and full-scale field verification studies, is at various stages of implementation, but over the next 5 years the research will be reported as criteria and guidance documents for user communities. The waste disposal research program will develop and compile a data base for use in the development of guidelines and standards for waste residual disposal to the land as mandated by the recently enacted legislation entitled "Resource Conservation and Recovery Act of 1976" (RCRA).

The current waste residual disposal research program has been divided into three general areas: (a) Design considerations for Current Landfill Disposal Techniques; (b) Alternatives to Current Landfill Disposal Techniques; and (c) Remedial Action for Minimizing Pollutants from Unacceptable or Inoperative Sites.

The waste residual disposal research program has been discussed in previous symposiums. See Schomaker, N.B. and Roulier, M.H., Current EPA Research Activities in Solid Waste Management: *Research Symposium on Gas and Leachate from Landfills: Formation, Collection and Treatment*, March 25-26, 1975, Rutgers, State University of New Jersey; and Schomaker, N.B., Current Research on Land Disposal of Hazardous Wastes: *Residuals Management by Land Disposal: Proceedings of the Hazardous Waste Research Symposium*, February 2-4, 1976, University of Arizona; and Schomaker, N.B., Current Research on Land Disposal of Municipal Wastes: *Management of Gas and Leachate in Landfills: Proceedings of the Third Annual Municipal Solid Waste Research Symposium* March 14-16, 1977, Universtiy of Missouri.

WASTE CHARACTERIZATION/DECOMPOSITION

The overall objective of this research activity is to provide information on the composition of municipal and hazardous wastes, the compatibility of hazardous wastes, and aqueous and gaseous emissions from disposed wastes. Sampling techniques, analytical methods, and techniques for determining emissions will be developed for implementing better disposal practices and waste management.

The initial effort (1) in the hazardous waste characterization area relates to the chemical composition, physical characteristics, and origin of hazardous wastes delivered to several Class I (hazardous chemical) landfills in the State of California. The average concentration, estimated daily decomposition, and partitioning of 17 metal species in hazardous waste landfills in the greater Los Angeles, California area was studied. Mass deposition rates were determined by calculating the average concentration of the metal species in conjunction with approximate daily volume received at the site. The effort has been published in a report entitled *A Case Study of Hazardous Wastes Input Into Class I Landfills* - EPA-600/2-78-064, June 1978.

Standard Sampling Techniques

Standard Sampling procedures, including collection, preservation, and storage of samples, do not exist for solid and semi-solid wastes. Hazardous wastes, both at the point of generation and the point of disposal, are not homogenous mixtures and, additionally, may range in consistency from a liquid, through a pumpable sludge, to a nonpumpable solid. Existing procedures for sampling liquid effluents and soils will have application but must be adapted to a variety of circumstances and, more importantly, field tested extensively before they can be advocated as "the" way to sample. Experience with sampling procedures is being accumulated as part of several on-going SHWRD projects.

The initial effort (1) in this sampling technique area relates to an activity for standardized methods for sampling and analysis of hazardous wastes. Specialized sampling methods have been developed for safe, reproducible, and representation sampling of such wastes in a wide variety of physical states, compositions, and locations. Methods of containment, handling and custody of waste samples have also been investigated.

Standard Analytical Techniques

Analysis of the contaminants within a waste leachate sample is difficult due to interfering agents. Existing instrumentation functions well in the analysis of simple mixtures at moderately low concentrations but interference problems can be encountered for complex mixtures at high concentrations (1 percent by weight and greater). In this range the sample cannot always be analyzed directly and commonly must be diluted and/or analyzed by the method of standard additions. Options are the development of standard procedures for diluting and accounting for errors introduced thereby or the development of instrumentation capable of accurate, direct measurements at high concentrations in the presence of potential multiple interferences. Existing USEPA procedures for water and wastewaters are often not applicable. Analytical procedures are being developed on an as-needed basis as part of the SHWRD projects. However most of this work is specific to the wastes being studied and separate efforts were required to insure that more general procedures/equipment would be developed.

The initial effort (1) has resulted in compilation of analytical techniques used for contaminant analysis. This effort has been published in a report entitled *Compilation of Methodology Used for Measuring Pollution Parameters of Sanitary Landfill Leachates*, EPA-600/3-75-011, October 1975, and SHWRD is currently finalizing a collaborative testing study (2) on leachate analyses. In this study, leachate samples were sent to 50 laboratories for analysis of specific parameters. The results will provide information on detection limits and precision for contaminants in leachate, using currently accepted methods developed for water and wastewater.

Another effort which is also being finalized, relates to the compilation and evaluation of current leaching tests methods. In this study (2) various available leaching tests are described and the methods utilized are evaluated in relation to their adaptability to field conditions. Also, as a part of the sampling technique activity, analysis of wastes has been developed as a four level scheme, which begins with field characterization followed by three levels of progressively more detailed and instrument intensive laboratory analysis.

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(1) Parenthesis numbers refer to the project officers, listed immediately following this paper, who can be contacted for additional information.

Standard Leaching Tests

In studying the potential environmental impact of contaminants, a standard leaching test is needed to assess contaminant release from a waste. Such a test must provide information on the initial release of contaminants from a waste contacted not only by water but also by other solvents that could be introduced in disposal. Additionally, such a test must provide some estimate of the behavior of the waste under extended leaching. The Office of Solid Waste (OSW) has funded the Industrial Environmental Research Laboratory (IERL), USEPA, a study (3) to procedures for determining whether a waste contains significant levels of toxic contaminants and whether a waste will release such contaminants under a variety of leaching conditions.

Validation of a Standard Leaching Test (SLT) has been initiated and funded in part by SHWRD.(2) The passage of the RCRA on October 21, 1976 and the imposing time restraints, necessitated developing an Interim Standard Leaching Test (ISLT) Existing leaching tests are being evaluated for those elements that may be of special benefit to the development of an SLT and at least three candidate ISLT's have been tested as part of the OSW/IERL project.

In conjunction with the ISLT, a genetic toxicity test for landfill leachates is being investigated.(2) This effort is being performed to rapidly and inexpensively ascertain the potential mutagenicity hazards of waste materials by examining the leachates to determine the feasibility of using short-term genetic assays to predict chemical mutagens.

Waste Leachability

The characteristics of leachates from hazardous wastes are being investigated in several different studies. The initial hazardous waste leaching effort (4) was patterned after a method developed by the International Atomic Energy Agency (I.A.E.A.) for leach testing immobilized radioactive waste solids. Translucent plexiglass columns were utilized and observations of flow patterns as well as possible biological activity were made. Five industrial sludges and five Flue Gas Desulfurization (FGD) sludges were investigated. This effort is basically completed and the final report is being prepared. An interim report entitled *Pollutant Potential of Raw and Chemically Fixed Hazardous Industrial Wastes and Flue Gas Desulfurization Sludges*, EPA-600/2-76-182, July 1976 has been published.

Another on-going waste leachability effort (5) relates to inorganic industrial waste where there is no appreciable biological activity. This testing program was designed to evaluate leaching and pollutant release under a variety of leaching conditions which may be encountered in one or more disposal situations and to develop a short-term leaching and soil interaction test. Five different types of leaching conditions were utilized which employed three varying pH leaching fluids, deionized water and municipal refuse leachate. A major consideration in the leaching behavior of wastes is time. Some wastes will not release appreciable amounts of contaminants until leaching has removed salinity or reserve alkalinity from the waste. Accordingly, the laboratory leaching test is extended over time. Successive extracts of a waste, which change in composition as the waste is depleted, are used to challenge a sequence of three soil batches that are graded in size to allow taking samples for analysis between each step and to compensate for extract absorbed by the soil. The laboratory leaching procedure allows simulating one to ten years of field leaching and soil interaction in about two weeks of laboratory extractions. The test has not yet been checked against field data.

POLLUTANT TRANSPORT

Pollutant transport studies involve the release of pollutants in liquid and gaseous forms from various municipal and hazardous wastes and the subsequent movement and fate of these pollutants in soils adjacent to disposal sites. Both laboratory and field verification studies at selected sites are being performed to assess the potential for groundwater contamination. The studies will provide the information required to (a) select land disposal sites that will naturally limit release of pollutants to the air and water and (b) make rational assessments of the need for and cost-benefit aspects of leachate and gas control technology.

The overall objective of this research activity is to develop procedures for using soil as a predictable attenuation medium for pollutants. Not all pollutants are attenuated by soil, and, in some cases, the process is one of delay so that the pollutant is diluted in other parts of the environment. Consequently, a significant number of the research projects funded by SHWRD are focused on understanding the process and predicting the extent of migration of contaminants (chiefly heavy metals) from waste disposal sites.

These pollutant migration studies are being performed simultaneously in the areas of hazardous wastes and municipal refuse. Several previous discussions of these efforts have been presented. See Roulier, M.H., Attenuation of Leachate Pollutants by Soils, presented at the *Management of Gas and Leachate in Landfills: Proceedings of the Third Annual Municipal Solid Waste Research Symposium*, March 14-16, 1977 University of Missouri.

Bibliography and State of the Art

The initial effort (5) in this area resulted in a completed bibliography entitled *Transport of Hazardous Substances Through Soil Processes - Volume I: Bibliography* ORNL-EIS-74-70 Part I and *Transport of Hazardous Substances Through Soil Processes - Volume II:* Pesticides - ORNL-EIS-74-70 - Part 2. It is expected that it will be made available through the national technical information service (NTIS).

A second effort (5) consisted of a review of information on migration through soil of potentially hazardous pollutants contained in leachates from waste materials. The results have been published in a report entitled *Movement of Selected Metals, Asbestos, and Cyanide in Soils: Applications to Waste Disposal Problems*, EPA-600/2-77-022, April 1977. The document presents a critical review of the literature pertinent to biological, chemical, and physical reactions, and mechanisms of attenuation (decrease in the maximum concentration for some fixed time as distance traveled) of the selected elements arsenic, beryllium, cadmium, chromium, copper, iron, mercury, lead, selenium, and zinc, together with asbestos and cyanide, in soil systems.

Controlled Lab Studies

The initial effort (5) is examining the factors that attenuate contaminants (limit contaminant transport) in leachate from municipal solid waste landfills. These contaminants are: arsenic, beryllium, cadmium, chromium, copper, cyanide, iron, mercury, lead, nickel, selenium, vanadium, and zinc. The general approach was to pass municipal leachate as a leaching fluid through columns of well characterized, whole soils maintained in a saturated anaerobic state. The typical municipal refuse leachate was spiked with high concentrations of metal salts to achieve a nominal concentration of 100 mg/l. The most significant factors in contaminant removal were then inferred from correlation of observed migration rates and known soil and contaminant characteristics. This effort will contribute to the development of a computer simulation model for predicting trace element attenuation in soils. Modeling efforts to date have been hindered by the complexity of soil-leachate chemistry. The results of this effort have been published in a report entitled *Investigation of Landfill Leachate Pollutant Attenuation by Soils* EPA-600/2-78-158, August 1978.

The second effort (5) in this area is studying the removal of contaminants from landfill leachates by soil clay minerals. Columns were packed with mixtures of quartz sand and nearly pure clay minerals. The leaching fluid consisted of typical municipal refuse leachate without metal salt additives. The general approach to this effort was similar to that described in the preceding effort except that (a) both sterilized and unsterilized leachates were utilized to examine the effect of microbial activity on hydraulic conductivity and (b) extensive batch studies of the sorption of metals from leachate by clay minerals were conducted. The results of this effort have been published in a report entitled *Attenuation of Pollutants in Municipal Landfill Leachate by Clay Minerals*, EPA-600/2-78-157 August 1978.

The third effort (6) relates to modeling movement in soil of the landfill gases, carbon dioxide and methane. The modeling movement has been verified under laboratory conditions. This effort has not focused on the impact of gases on groundwater, but considers groundwater as a sink for carbon dioxide. Results to date have involved design curves and tables which have been used to successfully evaluate a gas problem in Minnesota.

A fourth effort (5) relates to the use of large-scale, hydrologic simulation modeling as one method of predicting contaminant movement at disposal sites. The two-dimensional model that was used successfully to study a chromium contamination problem is being developed into a three-dimensional model and will be tested on a well-monitored landfill where contaminant movement has already taken place. Although this type of model presently needs a substantial amount of input data, it appears promising for determining contaminant transport properties of field soils and, eventually, predicting contaminant movement using a limited amount of data. A list of available simulation models has been developed which describes the advantages and disadvantages of these models for simulating landfill behavior.

A fifth effort (1) relates to organic contaminant attenuation by soil. This is our initial effort in organic contaminant movement in soil. Much more is known about inorganic contaminant movement in soil because the analytical techniques for inorganic materials are well developed and relatively cheap compared to the time-consuming analytical techniques for organic materials. The problem is compounded by the fact that organic contaminants are more numerous and more are being synthesized all the time. PCB is the organic contaminant currently being investigated. As a part of the above described effort, a gas chromatographic analytical procedures was developed that allowed improved quantitative measurement of PCB's in aqueous solutions.

A sixth effort (5) relates to an evaluation of the conditions that would control the movement of hexachlorobenzene (HCB) out of landfills and other disposal/storage facilities into the surrounding atmosphere. The potential for volatilization indicates a need for disposal site coverings that will reduce the vapor phase transport of HCB into the surrounding atmosphere. The volatilization fluxes of hexachlorobenzene from industrial wastes (hex waste) were determined using coverings of soil, water and polyethylene film in a simulated landfill under controlled laboratory conditions. Coverings of water and soil were found to be highly efficient when compared on a cost basis. Volatilization flux through a soil cover was directly related to soil air-filled porosity and was therefore greatly reduced by increased soil compaction and increased soil water content.

A seventh effort (5) relates to the adsorption, movement and biological degradation of high concentrations of pesticides in soils. Equilibrium adsorption isotherms were obtained for 2,4-D amine, atrazine, terbacil, and methyl parathion and four soils from different locations within the United States. Pesticide solution concentrations ranged from zero to the aqueous solubility limit of each pesticide. The mobility of each pesticide increased as its concentration in the soil solution phase increased. Pesticides degradation rates and soil microbial populations generally declined as the pesticide concentration in the soil increased.

Field Verification

Limited field verification is being conducted. The initial effort (4) to date has consisted of installing monitoring wells and coring soil samples adjacent to three municipal landfill sites to identify contaminants and determine their distribution in the soil and groundwater beneath the landfill site. The sites represent varying geologic conditions, recharge rates, and age, ranging from a site closed for 15 years to a site currently operating. Individual site characteristics were identified, and sample analyses necessary to determine the primary pollutant levels in the waste soils and groundwater were determined. The result os this effort are discussed in a report entitled *Chemical and Physical Effects of Municipal Landfills on Underlying Soils and Groundwater* EPA-600/2-78-096, May 1978.

A second effort (5) relates to the vertical and horizontal migration patterns, of zinc, cadmium, copper, and lead through the soil and shallow aquifer systems at a secondary zinc smelter. These patterns were defined using soil coring and monitoring well techniques. The migration of metals that occurred has been limited to relatively shallow depths into the soil profile by attenuation processes. Soil coring was determined to be an effective investigative tool, but not suitable by itself for routine monitoring of waste disposal activities. However, it should be used to gather preliminary information to aid in determining the proper horizontal and vertical locations for monitoring well design.

POLLUTANT CONTROL

Pollutant control studies are needed because experience and case studies have shown that some soils will not protect groundwater from contaminants. Even sites with "good soils" may have to be improved to protect against subsurface pollution. The overall objective of this research activity is to lessen the impact of pollution from waste disposal sites by technology that minimizes, contains, or eliminates pollutant release and leaching from waste residuals disposed of to the land.

The pollutant control studies are determining the ability of in-situ soils and natural soil processes to attenuate leachate contaminants as the leachate migrates through the soil from landfill sites.

Natural Soil Processes

The treatment by natural soil processes of pollutants from hazardous waste and municipal refuse disposal sites is being performed in the controlled lab studies previously discussed in the section on pollutant transport.

Liners/Membranes/Admixtures

The liner/membrane/admixture technology (4) is being studied to evaluate suitability for eliminating or reducing leachate from landfill sites of municipal or industrial hazardous wastes. The test program will evaluate, in a landfill environment, the chemical resistance and durability of the liner materials over 12- and 36-month exposure periods to leachates derived from industrial wastes, SO_x wastes, and municipal solid wastes. Acidic, basic, and neutral solutions will be utilized to generate industrial waste leachates.

The liner materials being investigated under the hazardous waste program include five admixed materials and eight polymeric membranes. The admixed materials are:

- Asphalt emulsion or nonwoven fabric (0.3 in)
- Compacted native fine-grain soil (12.0in)
- Hydraulic asphalt concrete (2.5in)
- Modified bentonite and sand (5.0in)
- Soil cement with and without surface seal (4.0in)

The eight polymeric membrane liners are:

- Butyl rubber, fabric reinforced (34 mils)
- Chlorinated polyethylene (32 mils)
- Chlorosulfonated polyethylene, fabric reinforced (34 mils)
- Elasticized polyolefin (20 mils)
- Ethylene propylene rubber (50 mils)
- Neoprene, fabric reinforced (32 mils)
- Polyester elastomer, experimental (8 mils)
- Polymeryl chloride (30 mils)

Specimens of these materials have been exposed for more than 2 years to the following six classes of hazardous wastes which utilized ten specific types of wastes: strong acid; strong base; waste of saturated and unsaturated oils; lead waste from gasoline tanks; oil refinery tank bottom waste (aromatic oil); and pesticide waste.

Preliminary exposure tests have been completed on the various liner materials in the various waste in order to select combinations for long term exposures. The results of these tests along with a discussion of the overall hazardous waste liner material program are presented in a report entitled *Liner Materials Exposed to Hazardous and Toxic Sludges First Interim Report*, EPA-600/2-77-081, June 1977.

A second effort (4) relates to a state-of-the-art of landfill impoundment techniques. This literature search surveyed the use of liner materials in impoundment sites for the containment of seven general types of industrial wastes. This data was supplemented with information obtained from various manufacturers, suppliers and installers and contains analyses of liner compatibility with industrial wastes.

A third effort (4) relates to the types of materials being tested for use as liners for sites receiving sludges generated by the removal of sulfur oxides (SO_x) from flue gases of coal-burning power plants. The volumes of SO_x sludge generated in any particular place will, typically, be much greater than those for other types of wastes, and therefore the disposal sites will be large. Consequently, methods of lining such disposal sites must have a low unit cost It is desirable that the materials be easy to apply or install. Because of these considerations, the number of polymeric membranes included in the study have been reduced whereas admixed and sprayed-on materials are being emphasized. A total of 18 materials are being tested with two types of Flue Gas Desulfurization (FGD) sludges. The sludges are from an eastern coal lime and limestone scrubbed process.

The liner materials consisted of admixed material, prefabricated membranes, and spray on materials. The admixed materials consisted of the following: cement; lime; cement with lime; polymeric bentonite blend (M179); gray powder-guartec (UF); asphaltic concrete; TACSS 020; TACSS 025; TACSS C400; and TACSS ST. The prefabricated membranes liner materials consisted of the following: elasticized polyolefin; black neoprene - coated nylon; and black neoprene - reinforced fabric. The spray-on liner materials consisted of the following: polyvinyl acetate; natural rubber latex; natural latex; polyvinyl acetate; asphalt cement; and molten sulphur.

For this above effort, a total of 72 special test cells were constructed to perform 12 and 24 month exposure tests. The 12-month exposure tests has been completed and the report is being prepared.

A fourth effort (4) relates primarily to the identification and description of waste disposal sites and holding ponds which have utilized an impermeable lining material. Also, three potential excavation techniques for liner recovery operations are described and discussed. This effort has been published in a report entitled *Liners for Sanitary Landfills and Chemical and Hazardous Waste Disposal Sites* EPA-600/9-78-005, May 1978.

Chemical Stabilization

Chemical stabilization is achieved by incorporating the solid and liquid phases of the waste into a relatively inert matrix which is responsible for increased physical strength and which protects the components of the waste from dissolution by rainfall or by soil water. If this slows the rate of release of pollutants from the waste sufficiently so that no serious stresses are exerted on the environment around the disposal site, then the wastes have been rendered essentially harmless and restrictions on where the disposal site may be located will be minimal.

The initial chemical fixation effort (4) relates to the transforming of the waste into an insoluble or very low solubility form to minimize leaching. The test program consists of investigating ten industrial waste streams, both in the raw and fixed state. The waste streams were treated with at least one of seven separate fixation processes and subjected to leaching and physical testing. The fixation process and sludge assignment matrix is shown below.

The lab studies have been completed and the field studies initiated. The laboratory leaching test data for the first 6 months includes: methods for physical and chemical analyses, documentation of various sludge fixation processes, and physical and chemical data on the sludges. The results have been compiled and discussed in a report entitled *Pollutant Potential of Raw and Chemically Fixed Hazardous Industrial Wastes and Flue Gas Desulfurization Sludges - Interim Report* EPA-600/2-76-182, July 1976.

The laboratory physical program test included physical properties (grain size distribution, atterbug limits, specific gravity, volume-weight-moisture relationships and permeabilities), engineering properties (compaction and unconfined compression) and durability properties (wet-dry and freeze-thaw) for both the raw and fixed sludges. The results of this effort have been discussed in a report entitled, *Physical and Engineering Properties of the Hazardous Industrial Wastes and Sludges,*

Sludge Category	Processes A	B	C	D	E	F	G
FGD, lime process, eastern coal	X	X	-	-	X	X	X
Electroplating	X	X	X	X	-	-	-
Nickel/cadmium battery	X	X	-	-	-	-	-
FDG, limestone process, eastern coal	X	X	-	-	X	+	X
FGD, double alkali process, eastern coal	X	X	-	-	X	+	X
FGD, limestone process, western coal	X	X	-	-	X	X	X
Inorganic pigment	+	+	X	-	-	-	-
Chlorine production, brine sludge	X	X	+	-	-	-	-
Calcium fluoride	X	X	+	-	-	-	-
FGD, double alkali, western coal	X	X	-	-	X	+	X

X = Sludge actually fixed by processor and placed in column.
+ = Sludge evaluated by processor but not fixed for this study.
- = Sludge not evaluated by processor.

EPA-600/2-77-139, August 1977.

The second effort (4) relates to a survey and identification of solidification/stabilization technology available in addition to those techniques currently being investigated. This effort consisted of examining six major categories of industrial waste fixation systems and discussing the advantages/disadvantages of each. The six categories are shown below:

- Cement - based techniques
- Lime - based techniques
- Thermoplastic techniques (including bitumen, paraffin and polyethylenes)
- Organic polymer techniques
- Self-cementing techniques

Another aspect of this effort consisted of listing and describing some 13 companies that solidify or fix hazardous wastes or sell fixation materials. The survey and identification have been completed and the report is being prepared.

The third effort (4) relates to a series of field verification studies to verify success with which pollutants have been immobilized at landfills receiving stabilized hazardous wastes. Four sites where stabilized industrial wastes had been disposed were examined to determine the effects of stabilized wastes on surrounding soils and groundwater. The sludges had all been fixed using the same proprietary process. Two of the industrial waste sites contained auto assembly (metal finishing) wastes, one site contained electroplating wastes and the fourth site contained refinery sludges. The physical properties of soils under the disposal sites were affected little, if at all, by the disposal operation.

A fourth effort (2) relates to a laboratory assessment of fixation and encapsulation processes for arsenic-laden wastes. Three industrial solid wastes that are high in arsenic concentration have been treated by generic processes in laboratory and by proprietary processes at vendors' facilities. Leaching studies on treated wastes consisting of Shake tests on pulverized samples and on intact monolithic samples are being performed to assess the relative safety of each product for disposal.

A fifth effort (7) relates to encapsulating process for managing hazardous wastes. This study consists of developing and evaluating techniques for encapsulating hazardous wastes. Techniques for encapsulating unconfined dry wastes are discussed in a report entitled *Development of a Polymeric Cementing and Encapsulating Process for Managing Hazardous Wastes*, EPA-600/2-77-045, August 1977. Additional evaluations are currently being performed whereby containers of hazardous waste (i.e., 55 gallon drums) are placed in a fiber glass thermo setting resin casing and the casing is covered with a high density polyethylene. Laboratory tests are being performed: to evaluate stresses encountered during storage, transport and disposal in a landfill; to leaching by water and HCL, and to mechanical tests to evaluate the ability to retain toxic materials. Also being evaluated is the use of cements for encapsulation of small containers.

Moisture Infiltration

Moisture infiltration is the primary mechanism which can control pollutant generation from landfills. This technology is being studied under an initial effort (4) which is developing a criteria matrix whereby the various functional requirements of cover material can be described and evaluated for each of the various soil types occurring in the U.S.A.

POLLUTANT TREATMENT

The overall objective of the pollutant treatment studies is to develop chemical, physical, and biological processes for treating landfill leachate once it has been collected and contained at the landfill site. Treatment by natural soil processes may be used at some sites where pollutant retention by soils is sufficient to allow uncontrolled release of leachate from the landfill into underlying soils.

Natural Soil Processes

The treatment of pollutants (5) from hazardous waste and municipal refuse disposal sites by natural soil processes has been described previously in the section on pollutant transport.

Physical-Chemical Treatment

The treatment of municipal refuse leachate (6) was evaluated in several laboratory studies using the following physical-chemical processes: chemical precipitation, activated carbon adsorption, reverse osmosis, ion exchange, ozonation, and chemical oxidation. The activated carbon was quite effective in removing refractory organics in the effluent of biological units. Results of the initial efforts have been reported in a journal article entitled, *Chemical Treatment of Leachates from Sanitary Landfills*, JWPCF, Vol. 46, No. 7, July 1, 1974, pp. 1776-1791 and in a report entitled *Sanitary Landfill Stabilization with Leachate Recycle and Residual Treatment*, EPA-600/2-75-043, October 1975. The expansion (6) of the initial efforts to include chemical oxidation, ion exchange and ozonation has been discussed in two reports entitled *Evaluation of Leachate Treatment: Volume I - Characteristics of Leachate*, EPA-600/2-77-186a, September 1977 and *Evaluation of Leachate Treatment: Volume II - Biological and Physical-Chemical Processes*, EPA-600/2-77-186b, November 1977.

A third effort (5) relates to a labbratory study of agricultural limestone and hydrous oxides of Fe. This study was performed to evaluate their use as landfill liner materials to minimize the migration of metal contaminants. Preliminary research on limestone and Fe hydrous oxide liners indicates these materials have a marked retarding influence on many of the trace elements. The limestone barrier showed the migration rate of all 12 metals studied and it was more effective in retention of some metals than others. However, the increased water contamination from solubilization of iron seems to rule out use of iron oxides until further work is conducted.

A fourth effort (5) relates to a laboratory evaluation of ten natural and synthetic materials (bottom ash, flyash, vermiculite, illite, Ottawa Sand, activated aluminia, cullite) for the removal of contaminants in the leachate and liquid portion of three different industrial sludges (calcium fluoride sludge, petroleum sludge, metal finishing sludge). This investigation involves beaker studies to evaluate the static adsorption capacity of sorbent materials using maximum background concentrations of contaminants in the leachate, followed by column studies to obtain information regarding the dynamic adsorption of leachate resulting from a calcium fluoride sludge. Results of the laboratory experiments indicate sorbent capacity is a function of the pH and concentration of the particular contaminant in the leachate with the volume of leachate that can be treated with maximum removal being regulated by the velocity through the bed. The information is discussed in a report entitled *Sorbents for Fluoride, Metal Finishing and Petroleum Sludge Leachate Contaminant Control*, EPA-600/2-78-024, March 1978.

Biological Treatment

Various unit processes for biological treatment of municipal refuse leachate have been investigated in the laboratory.

The results of this initial effort (6) have been reported in a journal article entitled, *Treatability of Leachate from Sanitary Landfills*, JWPCF Vol. 4, No. 6, June 1974, pp. 860-872. A second effort (6) has investigated the process kinetics, the nature of the organic fraction of municipal refuse leachate, and the degree of treatment that may be obtainable using conventional wastewater treatment methods. The biological methods evaluated were the anaerobic filter, the aerated lagoon, and combined treatment of activated sludge and municipal sewage. Biological units were operated successfully without prior removal of the metals that were present in high concentrations. The results of this effort are discussed in the same two EPA leachate treatment reports mentioned under the above physical/chemical treatment section.

Thermal Decomposition

Treatment by thermal decomposition relates to the establishment of time-temperature relationships for incinerating pesticides. Specifically, through the test program, existing information will be summarized into a state-of-the-art document and experimental incineration/decomposition studies will be conducted on approximately 40 pesticides. A lab scale evaluation/confirmation study and a pilot scale incinerator study are currently being performed.

The initial effort (1) related to the determination of incineration conditions necessary for safe disposal of pesticides. An experimental incinerator was constructed and utilized to determine the time-temperature conditions needed for the safe destruction of pesticides. This effort is discussed in a report entitled *Determination of Incinerator Operating Conditions Necessary for Safe Disposal of Pesticides*, EPA-600/2-75-041, December 1975. This research has been supplemented by another effort documenting in detail the various research projects relating to thermal destruction of pesticides. Efficiencies of combustion, residence time, and other parameters for safe incineration were documented. This effort is discussed in a report entitled *Summation of Conditions and Investigation for the Complete Combustion of Organic Pesticides* EPA-600/2-75-044, October 1975.

A second effort (1) relates to the development of laboratory scale methods for determining the time-temperature relationships for the decomposition of pesticides. A specialized laboratory system incorporating a two-stage quartz tube was utilized for determining the thermal destruction properties of pesticides and other hazardous organic substances. With this system, a small sample was first converted to the gas phase, then exposed to high-temperature destruction conditions in flowing air. With this system, high-temperature decompositions of Kepone, Mirex, DDT, and PCB's have been studied.

This effort has been discussed in two reports entitled *Laboratory Evaluation of High-Temperature Destruction of Kepone and Related Pesticides*, EPA-600/2-76-299, December 1976 and *Laboratory Evaluation of High-Temperature Destruction of Polychlorinated Biphenyls and Related Compounds*, EPA-600/2-77-228, December 1977.

CO-DISPOSAL

Presently, little is known on what effect adding industrial waste has on the decomposition process and the quantity and quality of gases and leachate produced during decomposition. The disposal of municipal and industrial sludges with municipal refuse may also influence the biologic decomposition processes. There is a concern that addition of industrial wastes, particularly those high in heavy metals, may inhibit biological activity and may result in elevated metal concentrations in leachate and potentially, in potable groundwater supplies. Conversely, because of the high moisture content and, commonly, the high pH and alkalinity of these sludges, microbial activity may be enhanced.

The overall objective of the co-disposal activity is to assess the pollution potential impact of the disposal of industrial waste materials with municipal solid waste. Therefore a project utilizing experimental landfill test cells was undertaken. Gas and leachate production characteristics are being used to determine the influence of selected sludges when added to municipal refuse.

The initial effort (6) involves a study whereby a combination of municipal solid waste and various solid and semi-solid industrial wastes was added to several field lysimeters. Material flows were measured and characterized for the continuing study and related to leachate quality and quantity, gas composition and production, and microbial activity.

The industrial wastes investigated were: petroleum sludge, battery production waste, electroplating waste, inorganic pigment sludge, chlorine production brine sludge, and a solvent-based paint sludge. Also, municipal digested primary sewage sludge dewatered to approximately 20 percent solids was utilized at three different ratios. Initial results of this effort are discussed in a paper entitled "The Effects of Industrial Sludges on Landfill Leachate and Gas," *Proceedings - National Conference on Disposal of Residues on Land*, September 1976, pp. 69-76.

A second effort (5) to assess the potential effects of co-disposal involves the leaching of industrial wastes in the laboratory with municipal landfill leachate as well as water. Results to date indicate that, when compared with water, municipal landfill leachate solubilizes greater amounts of metals from the wastes and promotes more rapid migration of metals through soil. The municipal landfill leachate is a highly adorous material containing many organic acids and is strongly buffered at a pH of about 5. Consequently, it has proved to be a very effective solvent.

This study examines only the solubilization of industrial waste by landfill leachate. In the landfill, the opportunity exists for retention of solubilized materials by the organic fraction of the municipal refuse. This will be evaluated in the field lysimeter study described above.

A third effort (4) relates to chemically treated and untreated industrial wastes being disposed of in a simulated municipal refuse landfill environment. Large lysimeters, six foot in diameter by twelve feet high, are being utilized to determine the difference in leachate quality between the treated and untreated wastes when mixed with municipal refuse. The industrial sludges selected for the study were calcium fluoride, chlorine brine production and electroplating. The sludges were chemically fixed by two processors. The material was allowed to cure as per the processors recommendations. Leaching data will be correlated with the laboratory leaching data to determine the benefits of co-disposing of treated wastes.

REMEDIAL ACTION

The Office of Solid Waste (OSW) has concluded the investigation of 391 damage cases. Fifteen percent of these cases involved groundwater pollution from hazardous waste landfills, 25 percent involved groundwater pollution from indiscriminate dumping practices, and 40 percent involved leachate problems. Nine percent or 35 of the 391 damage cases involved well pollution. In order to assist OSW in resolving this concern, this research activity was created with an overall objective to determine the best practical technology and economical corrective measures to remedy these landfill leachate and gas pollution problems. The initial effort (2) is to provide local municipalities and users with the data necessary to make sound judgments on the selection of viable, in-situ, remedial procedures and to give them an indication of the cost that would be associated with such a remedial project. This research effort consists of three phases. Phase I will be an engineering feasibility study that will determine on a site specific basis the best practicable technology to be applied from existing neutralization or confinement techniques. Phase II will determine the effectiveness, by actual field verification, of the recommendations/first phase study. Phase III will provide a site remedial guide to local municipalities and users. A guidance manual is currently being prepared which will assist the user community in the selection of available engineering technology to reduce or eliminate leachate generation at inoperative landfills. Five categorical areas are discussed: Surface water control, groundwater control, plume management, chemical immobilization and excavation/reburial.

LANDFILL ALTERNATIVES/LAND CULTIVATION

Waste materials are primarily deposited in sanitary landfills or incinerated. Because of concern for environmental impact and economics, other landfill alternatives have been proposed. For SHWRD purposes, the alternatives currently being considered are: (1) deep well injection, (2) underground mines, (3) land cultivation, and (4) saline environments. The overall objective of the landfill alternatives study is to determine the feasibility and beneficial aspects of these techniques by assessing the environmental impact and economics.

Deep Well Injection

The first effort (7) consisted of a review and analysis of available information related to deep-well injection, and an assessment as to the adequacy of this method for managing hazardous wastes and ensuring protection of the environment. The study provided a comprehensive compilation of available information regarding the injection of industrial hazardous waste into deep wells. This effort has been discussed in a four volume report entitled, *Review and Assessment of Deep-Well Injection of Hazardous Waste*, Volumes I-IV, EPA-600/2-77-029 (a-d), June 1977.

A second effort (5) provided detailed information on the application of deep well injection technology. Local geologic and hydrologic characteristics of the injection and confining intervals are considered along with the physical, chemical and biological compatability of the receiving zone with the wastewater to be injected. Design and construction aspects of injection wells are presented along with recommended pre-injection testing, operating procedures, and emergency precautions. This effort is discussed in a report entitled, *An Introduction to the Technology of Subsurface Wastewater Injection*, EPA-600/2-77-240, December 1977.

Underground Mines

The initial effort (7) consisted of a review and analysis of information of the placement of hazardous waste in mine openings. The study assessed the technical feasibility of storing nonradioactive hazardous wastes in underground mine openings. The results showed that a majority of the wastes considered can be stored underground in an environmentally acceptable manner if they are properly treated and containerized. This effort is discussed in a report entitled *Evaluation of Hazardous Wastes Emplacement in Mined Openings*, EPA-600/2-75-040, December 1975.

A second effort (4) related to an economic evaluation of storing non-radioactive hazardous wastes in a typical room and pillar type salt mine. The results include capital and operating costs and a cost analysis. The cost study was based on a simulated waste characteristic and conceptual design of the waste receiving, treatment, containerization, and underground storage facilities. This effort is discussed in a report entitled *Cost Assessment for the Emplacement of Hazardous Materials in a Salt Mine*, EPA-600/2-77-215, November 1977.

Land Cultivation

The disposal technique of land cultivation, whereby specific waste residues have been directly applied or admixed into soils, has been an alternate disposal option for many years by pharmaceutical, tannery, food processing, paper and pulp, and oil refinery industries. The soil environment can assimilate most types of organic waste by processes of adsorption, dilution, biodegradation, and oxidation. The initial effort (4) relates to gathering and assessing available information on land cultivation of hazardous industrial sludges with emphasis on characterization of waste types, quantities, operational technology, economics and environmental impacts. The results of this initial effort are discussed in two reports entitled, *Land Cultivation of Industrial Wastes and Municipal Solid Wastes: State-of-the-Art Study Volume I - Technical Summary and Literature Survey*, EPA-600/2-78-140a August 1978 and *State-of-the Art Study Volume II - Field Investigation and Case Studies*, EPA-600/2-78-140b August 1978.

The second effort (4) is a combination laboratory, greenhouse and field study to determine the fate and mobility of wastes in soil for the purpose of developing criteria for use in the design, management and monitoring of land cultivation disposal operations Decomposition rate, application rate, plant survival and growth, pollutant runoff and leachate generation will be obtained in development of the data base.

The third effort (4) relates to detailed field surveys and limited laboratory field experimentation for the purpose of developing a matrix of industrial organic and inorganic and municipal waste streams versus operational parameters. This matrix of information will be used to develop design and guideline criteria.

The fourth effort (8) relates to the

pit disposal method for excess pesticides as generated by farmers and agricultural applicators. Experimental systems have been developed to investigate the fate of selected pesticides in isolated micro-pits under controlled conditions. The chemical and biological consequences of pit disposal of dilute insecticides, fungicides, and rodenticides are being determined.

Saline Environment

This saline environment effort relates entirely to municipal solid wastes and therefore will not be discussed in detail at this symposium. This effort is primarily a paper study detailing the present environmental and economic status of this type of disposal option. It will be supplemented by case histories and state regulations and policies in effect for those states bordering saline waters.

ECONOMIC/ENVIRONMENTAL IMPACT

The use of market-oriented incentive (disincentive) mechanisms has received very scant consideration for pollution control policy in the United States, particularly in the area of hazardous waste management. Economic theory suggests that incremental pricing of waste collections and disposal would reduce the waste generation rate, enhance source separation of recyclable materials, accelerate technological innovation, and minimize total system cost.

The economic relevance is being addressed to hazardous waste management in general and the environmental impact aspect is being addressed to Flue Gas Cleaning (FGD) sludge disposal.

In the economic relevance effort (9) currently being investigated, a methodology is being developed that permits economic and social impacts of alternative approaches to hazardous waste management to be addressed. The procedure involves generation of a series of environmental threat scenarios that might arise from the use of different hazardous waste management techniques. The costs attributable to any technique comprise the control costs, and the environmental costs and benefits together determine the net benefits associated with the threat scenarios.

In the environmental impact effort (2) the problem of FGD sludge disposal to the land has been addressed. This effort considered the problem from a potential regulatory approach by evaluating the existing data base and projecting its potential impact on the promulgation of sludge disposal regulations. This effort has been published in a report entitled *Data Base for Standards/Regulations Development for Land Disposal of Flue Gas Cleaning Sludges*, EPA-600/7-77-118, December 1977.

CONCLUSION

The laboratory and field research project efforts discussed here reflect the overall SHWRD effort in hazardous waste disposal research. The projects will be discussed in detail in the following papers. More information about a specific project or study can be obtained by contacting the project officer referenced in the text. Inquiries can also be directed to the Director, Solid and Hazardous Waste Research Division, Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, 26 West St. Clair Street, Cincinnati, Ohio 45268. Information will be provided with the understanding that it is from research in progress and that conclusions may change as techniques are improved and more complete data become available.

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All the Project Officers, except for Mr. Michael Gruenfeld, are associated with the Solid and Hazardous Waste Research Division (SHWRD), whose address is shown above.

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INDUSTRIAL HAZARDOUS AND TOXIC WASTE PROGRAM OF EPA's INDUSTRIAL POLLUTION CONTROL DIVISION - IERL-CI

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ABSTRACT

The Industrial Pollution Control Division has responsibility for research into control of all pollutants (air, water and solid waste) from the following type of industries: (1) organic chemicals, (2) inorganic chemicals, (3) nonferrous metals, (4) food, (5) wood and wood products and (6) miscellaneous industries related to these. The program is an integrated multimedia approach to these problems and ranges from assessment to ultimate disposal and economical reuse of waste materials. The assessment program identifies potentially hazardous pollutants from these industries and methods of solution are then sought. This paper discusses the portions of this program relating to the disposal, detoxification and reuse of hazardous wastes from these industries. The ultimate disposal and resource recovery portions of the program are given particular emphasis.

INTRODUCTION

The Industrial Environmental Research Laboratory (IERL) is a new addition to the office of Research and Development of EPA. It was formed out of parts of earlier EPA entities, including a portion of the Industrial Wastewater Treatment Laboratory in Edison, New Jersey, a portion of the National Environmental Research Center in Corvallis, Oregon, and other groups throughout the country. The IERL-CI is one of two such laboratories, the other being in Research Triangle Park, North Carolina.

These laboratories are unique in the EPA, in that rather than dealing strictly with air and water pollution or solid waste generation and disposal, they deal with the industries and their pollution problems on a multimedia basis. As a result, the two laboratories' programs are split along industry lines rather than medium lines. For example, the IERL-RTP has responsibility for the Ferrous Metals Industry. While the IERL-Cincinnati has responsibility for the Nonferrous Metals Industry. Similarly, in the Organics area, IERL-RTP assumes responsibility for Petroleum Refining while Cincinnati has responsibility for the production of Industrial Organic Chemicals and related processes. As can be seen, there is a great deal of overlap between the program, so close cooperation between the laboratories is essential.

The IERL, Cincinnati consists of three Divisions, The Resource Extraction and Handling Division (REHD), The Energy Systems Environmental Control Division (ESECD), and the Division, which I will be talking about today, - The Industrial Pollution Control Division (IPCD).

The IPCD is made up of three Branches. The Organic Chemicals and Products Branch (OCPB), The Metals and Inorganic Chemicals and Products Branch (MICB), and the Food and Wood Products Branch (FWPB). Each Branch has the responsibility to investigate multimedia pollution from the industries under its jurisdiction. The program while considering all the classical pollutants such as COD and BOD in water, and particulate, nitrogen oxide, etc. in air, is mainly concerned with the control of toxic and hazardous materials in each of these media. As a result, it is often difficult to separate the solid waste aspects of the program, especially when dealing with the measurement of pollutants or identification of the type of waste.

The IPCD's program is broken up into three general categories:

1. Industry assessment
2. Control equipment and disposal technology development and evaluation
3. Control equipment and disposal technology demonstration

Becasue we were one of the first groups in EPA to start looking at industries as units rather than as individual sources of pollutants, the principal portion of our program to date has been in the assessment area. These assessments are multimedia and are generally done on a full industry. Some of these that have been done or are in the latter stage of completion are:

1. Secondary Nonferrous Metals Industry
2. Pharmaceutical Industry
3. Compounding and Fabricating Industries

These industries were chosen partly because it was felt that they were complex enough that they should be looked at as a unit, and partly in order to satisfy the pressing needs of various EPA program offices, especially the Effluent Guidelines Division and the Office of Air Quality Planning and Standards. When these assessments were started it was quickly realized that many studies of the individual industries were either completed or were under way. Typically, these studies addressed only one aspect of an industry, such as air pollution, water pollution, energy, or regulatory investigations. A review of the situation led to the decision that an overall industry assessment was needed to collect all available information. Over the succeeding months, past studies were extended and integrated. Many single media oriented research, demonstration, and development programs were assembled into a multimedia approach which then resulted in the skeleton for the assessment. Next the data was examined in the light of defining what does the industry look like, what are its bounds, what are the major processes of it, and what are the likely potential environmental impacts from it. The emphasis on the last was generally placed on potentially toxic and hazardous substances being emitted in any one of the three pollutant media.

Each production process or (in the case of the very complex industries such as the Organic Chemicals or Pharmaceutical Industries) some representative processes are described in the following terms:

1. Function
2. Feed materials
3. Operating conditions (temperature, pressure, etc.)
4. Utility requirements
5. Waste streams
6. Pollution control technology
7. Occupational and health effects

Obviously, we would often find that much of this data, especially the health and ecological effect data is just not available. In addition, we found with some industries that industry secrecy prevented a complete description of processes involved. In fact, with some industries we could not even obtain the total tonnages of product produced because of various confidentiallity requirements of the companies involved.

The next step of the assessment involves a detailed engineering analysis of the production processes in the industry. This analysis is performed for three primary reasons:

1. To identify obscure discharges
2. To determine if closer attention should be given to a unit operation that has traditionally been ignored or considered only a limited environmental problem
3. To predict the quantity and character of the discharges in each of the three media associated with each unit operation, based on the materials processed production capacity, and process conditions.

The engineering analysis is conducted by senior engineering personnel. Often little quantitative information is available on the discharges from many industrial processes. Therefore, a process-by-process analysis must be made of inputs, outputs, and operating conditions to determine the presence of unidentified potentially hazardous substances.

The engineering analysis is followed

by an in depth analysis of the same nature, once again relying on engineering know how of the senior staff doing the analysis. In this way the assessment study hopes to identify the industry and its potential for pollution.

The study then goes through a series of reviews by various experts in the field as well as the industry involved and culminates in the establishment of a computerized data base on the industry. This data base includes location of plants, products, (where available), production rates, pollutants involved, etc. Such a data base has been established for the Organic Chemicals Industry and the Pharmaceutical Industry and it will be also established for the plastics and synthetics, inorganic chemicals and the pigments and dyes industries.

As can be seen, the assessment work is quite complicated and can be expensive. The second phase, the control equipment or disposal technology development phase is of course the area in which the attendees of this conference are most interested. This phase is just getting under way. The IPCD has identified a number of waste streams that do need a great deal of attention, and we now are examining various technologies for their control and ultimate disposal. Currently the IPCD's emphasis is mainly in the development of sound disposal or destruction programs for such waste, and where economical processes for this can be identified (and economics is the key to this) recovery processes for organic materials and heavy metals.

In dealing with a hazardous material we feel the best choice is actually destroying it rather than placing it in a landfill where it may end up being just stored for a long period of time. Because of its common use, incineration is an obvious alternative to landfilling for many such cases. It is a well established technique and, when properly done, eliminates the hazard rather than just storing it for tomorrow. Unfortunately, as the Agency's experience with the disposal of Kepone, PCB's and other such materials and sludges have shown, there is no real way of knowing, prior to actual test burns, that a given incinerator can safely destroy a particular waste. A lengthy and expensive field testing procedure is required for the incineration of a given hazardous material.

The problem was well illustrated by the approach being used to dispose of Kepone and Kepone-contaminated residuals. Initially, little was known about the thermal destruction characteristics of Kepone so samples were sent to the University of Dayton Research Institute for a laboratory scale thermal decomposition analysis of the material. This work was done by Duval and Ruby who will be giving a paper on this later today. Their work determined that at too low a temperature, Kepone can produce hazardous substances upon decomposition. They established that at sufficiently high temperatures Kepone could be destroyed to relatively harmless substances.

Having predicted the ideal behavior of the compound, it was necessary to go to pilot scale studies. Based on these extensive very complicated studies involving a great deal of precautions (Dick Carnes will be discussing this later) a large incinerator was proposed to destroy the wastes. Even after this incinerator has been built, it will no doubt require extensive testing and modification before it can be used on an operating basis to destroy the large Kepone stocks stored there (if past experiences are a good indicator).

The problem is that no method of scaling up incinerators exist. Because of a lack of design criteria, one cannot say that if one incinerator works that another unit will do the job as well. While there are rough guidelines for doing this they are often inaccurate and their implementation is very expensive. Such a situation may be tolerated when a non-hazardous material is being destroyed, but with hazardous substances one does not have that maneuverability. It is necessary to establish whether a given incinerator can safely destroy a waste without going through the time and expense occurred in the above mentioned Kepone work. This is a long-term program and it is hoped that with time we can approach such idealizations.

The program has four parts:

1. Laboratory scale waste and composition studies
2. Development of general guidelines for incinerator design similarity criteria
3. Verification of these criteria through the use of non-hazardous wastes
4. Verification with hazardous waste incinerator in existing facilities

The Laboratory scale decomposition studies are a continuation of the Duval and Ruby work done under sponsorship of the Municipal Environmental Research Laboratory under Dick Carnes. We have joined the MERL, in the project with the University of Dayton Research Institute so that a Gaschromatograph Mass Spectrometer system could be purchased for the analysis of the decomposition products. The IPCD's main interest in this project is the establishment of what we term a "center of expertise" which would be available to us to respond to emergency conditions as they arise. For example, should we be asked to assist either program office or an industry in their effort to dispose of a hazardous material or waste, we could use the facilities at UDRI to characterize its thermal decomposition properties and potential products of decomposition. It could then be determined what the potential dangers are in its improper incineration and what temperatures are necessary for its proper incineration.

The second phase of our program, Development of General Guidelines for Incinerator Design, will translate the laboratory data to a specific incinerator design. It will basically establish residence time-temperature distribution profiles for different units of the same design and will result in some generalized scale up criteria to enable one to attempt at least to answer the question "if this material is properly disposed of in this small incinerator, what dimensions, burner configurations, etc. does a full scale unit need in order to do the same job." The first phase of this work is currently being done for the IERL, Cincinnati by TRW in Redondo Beach, California. The last two portions of this program are still in the planning stages. They are of course dependent on the results of phase 2 but in general they will consist of major sampling and analysis programs to verify the applicability of whatever generalized design criteria are established.

As an adjunct to our somewhat theoretical, incineration program, the IPCD is initiating a major program in the destruction of hazardous materials, especially chlorinated hydrocarbons, in cement kilns. This work is based on the fine work done by Skinner of Environment Canada and McDonald of St. Lawrence Cement in 1976, '77 on the disposal of chlorinated hydrocarbons in cement kilns. The work that they did showed that the process is technically feasible, however there is an acceptance problem by local citizens which must be overcome before the system can be implemented.

This problem is very similar to the one encountered in the siting of landfills or other refuse disposal facilities and is compounded by the fear of substances which are called "hazardous." The IPCD's program in this area, which is in conjunction with the Energy Systems Environmental Control Division, will be a two-year effort. The first phase which is now in the final stages of negotiation, will involve the burning of a non-hazardous chlorinated hydrocarbon in the cement kiln. This will involve sampling at the exhaust for the hydrocarbon as well as for the by-products produced in the partial decomposition material as determined by the University of Dayton Research Institute facility. Once destruction of this inocuous material is established, the work will shift towards more hazardous substances-culminating in the destruction of PCB's in the kiln.

This project is rather unique in that it is a joint project between a private cement company, a state agency, and U.S. EPA. It also has the interest and full cooperation, to date, of the County Department of Health, and representative of several environmental groups in the areas. By keeping everything "above board" and in the open and by following procedures laid out by the Office of Solid Waste in the selection of sanitary landfills, it is hoped that citizens acceptance of the technique will take place.

Another area where the IPCD is getting involved is the treatment of various industrial wastes, especially sludges for the purposes of reclamation of useful materials. This objective which has been investigated by a number of people, has often been a technical success and an economic failure. As a result our approach to this is very cautious. There is no question that there are many very specific waste streams which can be reclaimed; because of our process-by-process approach to the industries we deal with (as described in the assessment area description) we are approaching the reclamation concept on that basis. An area where such work looks promising is in the reclamation of ethylene glycol and antimony from polyester stillbottoms. Currently polyester stillbottoms are incinerated or disposed of at sea. However, these materials are quire toxic, containing large amounts of antimony catalyst used in the process, and an alternative to these disposal techniques is very desirable. We were recently approached by a University who has been in contact with a company that has developed and patented a rather simple process by which these stillbottoms could be depolymerized to the basic monomiers, and these as well as the antimony oxide be recovered for reuse. Because of the nature of these stillbottoms, they are concentrated in relatively small areas of the country, and the fact that the process involved is very cheap and easy to use, the recovery of useful materials from these looks very attractive. A proposal has been submitted to us and is now being evaluated for funding.

Should this project prove successful, (I have seen an actual demonstration of the process which is very simple) it will turn a hazardous waste material into a profit center and a source of useful raw materials.

Another project is currently ongoing in which industrial PVC scrap is reclaimed using a solvent process. The process is currently being developed on a laboratory scale and the properties of the recovered PVC and plasticizers are being evaluated. Future funding of this project is dependent on results of the lab scale phase.

In summary, the Industrial Pollution Control Divisions program for the measurement, reduction, and reuse of hazardous waste materials is just getting under way. Rather than being geared to the disposal of hazardous substances in general it is aimed at the solution of specific industrial problems as they arise and with an eye towards the processes producing the problems, rather than towards the solution of problems as independent entities.

References:

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2. McDonald, L.P. & Skinner, D.J., Burning Waste Chlorinated Hydrocarbons in a Cement Kiln, Technology Development Report #EPA 4-WP-77-2 Water Pollution Control Directorate Environment Canada, March 1977.

TEXAS' SOLID WASTE MANAGEMENT ACTIVITIES--AN OVERVIEW*

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ABSTRACT

The Texas Solid Waste Disposal Act assigns the solid waste regulatory jurisdiction to the Texas Department of Water Resources for industrial wastes and to the Texas Department of Health for municipal wastes. The term "industrial solid waste" is defined so as to include waste materials in liquid form, or suspended in liquids, and effectively, all other waste produced by a given industrial activity, except emissions to the air and wastewaters discharged or injected as authorized by Texas Department of Water Resources permit. Pursuant to this statute, the Texas Water Quality Board adopted an Industrial Solid Waste Management Regulation, Order 75-1125-1, to address multi-faceted problems existing in the field of industrial waste collection, handling, storage, and disposal. The Act limits the agency's authority over on-site disposal of solid waste to the adoption of rules, regulations, and guidelines. However, recent amendments to the Texas Solid Waste Disposal Act and Department rules require permits for on-site disposal of waste determined to be hazardous pursuant to federal rules.

The regulations established uniform requirements for all solid waste disposal sites, a shipping control system for off-site disposal, and a reporting system. The concept utilized provides general limitations stated in direct terms and leaves industry wide discretion in developing methodology to meet the limitations. Development of this regulation included consideration of numerous alternatives to the approach adopted. Future developments will be subject to experience gained in operating under the present regulation and changes in state and federal solid waste statutes.

*Manuscript of the paper not received in time for publication.

SOLID WASTE RESEARCH ACTIVITIES IN CANADA

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ABSTRACT

In Canada, industrial and hazardous waste management, including land disposal, is generally a private sector responsibility controlled by provincial government legislation and regulation. To date, the Federal government's role has been to develop and demonstrate appropriate technology and to develop guidelines or codes of good practice relating to various waste management aspects. These activities are conducted on a national basis in co-opertion with the various provincial govenment agencies.

Current research activities relating to land disposal of industrial and hazardous wastes are underway in the following study areas:

a) Special waste disposal;
b) Contaminant migration and attenuation;
c) Disposal site evaluation;
d) Landfilling procedures;
e) Waste exchange.

Some of the specific projects being conducted in each of these study areas by the Waste Management Branch, as part of our landfill research program, are discussed in this paper.

INTRODUCTION

This presentation deals only with the research activities relating to industrial and hazardous waste disposal as conducted by the Waste Management Branch of our federal government's Department of Environment. There are other research activities being carried out in Canada at the provincial government levels, as well as by various research institutes, universities and consultants. However, their activities are not discussed here unless they are under contract to the Branch.

One of the Waste Management Branch's responsibilities is to conduct research activities on a national basis. Development and demonstration of new or improved technology, and the subsequent development of guideline documents, based on our new understanding of the state-of-the-art, is undertaken to assist our provincial governments and the public in general to come to grips with the many "high profile" issues of industrial waste management.

The efforts of the Hazardous Waste Management Division within the Branch are directed primarily towards:

- land disposal research, with

some work also being done on incineration and waste exchange as disposal alternatives;
- inventory work to derive an accurate picture of waste generation; and
- guideline or policy development.

Current land disposal research activities may be divided into the following broad study categories:

- special waste disposal;
- contaminant migration and attenuation;
- disposal site evaluation;
- landfilling procedures.

Some of the specific projects in each category will be mentioned.

PCB ATTENUATION IN SOILS

Laboratory scale experiments were performed at the University of Waterloo to examine the attenuation of Aroclors 1016 and 1254 in soil. Three soils were used including sand, sandy silt and clayey silt.

Techniques were developed for: the extraction of aroclor from aqueous samples; the concentration of aroclor in solvents; and, the measurement of aroclor concentrations using gas chromatography with electron capture detection.

The experimental programme involved the use of teflon soil-waste reactors, which exhibited no apparent aroclor sorption.

Aqueous working solutions of Aroclor 1016 and 1254 were prepared. Unfortunately, the Aroclor 1254 was poorly soluble in water to the extent that its aroclor content could not be distinguished from background interference. This served to negate the results obtained from the subsequent Aroclor 1254 - soil contact experiments.

Aroclor-soil contact experiments were performed using two working solutions and three soils. The results showed that the Aroclor 1016 was removed from the aqueous phase in excess of 90% by weight in most cases. The stability of the Aroclor 1016 removal was tested in a series of desorption experiments. The results generally indicated that the sorption of the Aroclor 1016 was only slightly reversible under the conditions used.

The results of our study, and the indications from other studies that Aroclors are generally immobile within the soil system, might indicate that controlled disposal of PCBs in a municipal landfill, may be a feasible disposal alternative for PCB containing wastes. Such a landfill would provide retention times, allowing for the possible biodegradation of the aroclors, and it would also provide a variety of opportunities for sorption to occur within the fill itself. Any PCBs which might eventually be discharged from the landfill would be quickly sorbed and thereby retained onto the underlying soils.

SEPTIC TANK SLUDGE LANDFILLING

Earlier work carried out at the University of British Columbia on the effects of adding septic tank pumpings to municipal refuse indicated that additions could be beneficial in reducing both the peak concentrations and the total mass discharged of trace and heavy metals in the leachate. This work indicated, however, that relatively large amounts of septic tank pumpings had to be added to achieve the desired effect.

The main purpose of the follow-up research was to determine the optimum amount of septic tank additions to landfill, under varying conditions of net infiltration, refuse depth, and sludge additions. The septic tank sludge additions ranged from a relatively small amount to an amount approaching the estimated field capacity of the refuse.

The results have shown that significant reductions, both of peak concentrations and total mass, of contaminants discharged can be achieved by adding sludge to refuse under low precipitation infiltration conditions. This is particularly true of most metals. While the optimum amount of sludge to be added was not consistent in all cases, the trend is toward better reductions at high loadings, with lower loadings sometimes creating a detrimental effect. It was generally found that a minimum ratio of sludge addition should be 16,000 mg septic tank sludge solids per kg. of dry refuse.

Specific reasons for the preceding behaviour are difficult to provide for each of the contaminants. The final report, soon to be issued, discusses many possible explanations.

It was also found that no positive fecal coliform counts were ever obtained from the leachate, and that increasing the rate of infiltration tends to counteract some of the benefits obtained. In virtually all cases, self attenuation within the fill increased with increasing fill depth.

BORDEN LANDFILL STUDY

The detailed Camp Borden landfill leachate migration study, discussed at last year's research symposium, is now being extended to more specifically focus on the behavior of certain contaminants. In addition, a very extensive modelling effort is underway using the excellent field data complemented by more exact numerical field values of the various model coefficients.

Although the Borden data was made available to any modelling group for their own use, no requests for specific information have been received. The University of Waterloo work should, therefore, be a significant singular advancement of the state-of-the-art.

MISSISSAUGA LANDFILL STUDY

A 2 year study has been completed at this 78 acre site near Toronto which has served as a mixed municipal and industrial waste disposal site. The site was well instrumented upgradient, downgradient, and through the landfill, and routinely monitored.

Detailed chemical analyses were conducted including determinations of pesticide and PCB concentrations. At this site, the contaminant plume, as defined by chloride concentrations, has migrated about 3,000 feet through surficial sands and gravels.

Two mathematical models were utilized to simulate both the flow and mass transport at the site. The resulting downgradient concentration profiles were then used to predict a contaminant loading to a nearby receiving stream up to the year 2000.

A final report on this work should be available in the next few months. In the meantime, the modelling techniques are already being applied in landfill design work in Ontario and the U.S.

HAZARDOUS WASTE DISPOSAL SITE STUDY

As part of an evaluation of special waste management in the National Capital Area, a chemical landfill site was monitored to evaluate its environmental impact.

The site was found to be next to an old landfill, and it is known that toxic wastes have been discharged at the site for at least 18 years. The site is used to dispose of about 10 tons per year of miscellaneous toxic and hazardous inorganic and organic chemicals.

Although our investigations are still incomplete at this time, the very preliminary indications show no evidence of any nearby drinking water contamination either from the old landfill or the special waste disposal operation. The soils underlying the area are characterized as sands and gravels.

PCB SPILL SITE

A study is underway at a spill site in Regina to investigte the mobility of the transformer fluid containing PCBs. Soil samples have been extracted from the site in a first attempt to determine the extent of the contaminated soil.

Samples will also be used to conduct extraction and resolubilization tests. Some useful data should be in hand within four months, and a further in-depth investigation of PCB migration at the site will likely result.

PROCEDURES DOCUMENTS

Starting in 1975, the Branch initiated a series of international roundtable discussions on various technical aspects of landfilling. Participants were selected from among the top experts, including researchers, government personnel, and consultants in Canada and the U.S.

Our first session dealt with landfill leachate analysis, and was attended by a handfull of Canadian and U.S. scientists, including EPA sponsored contractors. Since then we have had sessions on ground water and soil sampling procedures, landfill monitoring programme design and implementation procedures, landfill gas control procedures, landfill leachate control procedures, and our next session on landfill leachate treatment will be held this April. Each session has been documented and results in the publication of specific procedures documents containing recommendations of a practical nature based on the consensus of opinion.

To date the documents have been well received in many countries, and the popularity of the sessions has increased greatly.

DISPOSAL GUIDELINES

Specific guideline documents dealing with particular waste disposal problems are being prepared. We have developed a draft copy of a guideline document dealing with wood waste disposal, as a first effort.

It is known that wood waste landfill leachate can be very toxic when fresh, and some data indicates a continued toxicity of leachate even from aged bark, sawdust, and shavings. Special precautions are therefore necessary in the disposal of such wastes in bulk quantities. The guideline document will address land disposal accordingly, in light of current waste-soil interaction information.

Another separate document is being prepared for arsenic bearing wastes. This document will provide a waste generator or discharger information on the nature of the wastes, its general behavior in the environment, and recommendations for the land disposal of the waste, based on the soils capabilities to attenuate the contaminants at the site.

This document will be followed by others. It is anticipated that the land disposal of PCBs and mercury will be addressed next.

OTHER RESEARCH ACTIVITIES

Other research activities relating to industrial and hazardous waste disposal include:

1) our continued work on developing a soil-waste matrix procedure for assessing the environmental suitability of a proposed industrial waste disposal site;
2) a study on the treatment of landfill leachate discharging from pulp mill disposal sites, by leachate recirculation;
3) a study on the treatment of leachate from a co-disposal site by aerobic biological treatment, and
4) a study attempting to develop a mathematical model to predict leachate characteristics under varying landfill operating conditions, using over 65,000 pieces of data routinely collected by several investigators over a period of almost 5 years.

Aside from land disposal research activities, our other efforts have been directed towards testing the burning of pesticides and PCBs, conducting inventory studies, and developing PCB management guidelines.

WASTE EXCHANGE

Last, but not least, is our waste exchange operation. We have recently given birth to a nation-wide exchange, operated by the Ontario Research Foundation in accordance with the recommendations for a methodology contained in a report prepared under contract to us.

The operation is being sponsored for a period of two years by ourselves, after which it should, if successful, become self-supporting.

The exchange has solicited listings

and will be generating bulletins once every two months. Listings in our January bulletin are from all parts of Canada. In addition to listing wastes available and wastes wanted, the bulletin also lists services available for transportation and reprocessing.

During the two year sponsorship period, the contractor will evaluate several aspects of a waste exchange operation, including the possibility of making a passive exchange more active, regionalizing the operation, and instituting exchanges across the border.

Should you want more information on the waste exchange operation, or on any of the other projects briefly mentioned, please contact the author.

KEPONE: AN OVERVIEW

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ABSTRACT

The serious environmental contamination of the manufacturing facility, sewage treatment works, and nearby environs of Hopewell, Virginia, by the pesticide Kepone required a sound technical approach to disposal options and a public awareness program stretching from Hopewell to Toledo, Ohio. Background data were developed for the thermal stability of the Kepone molecule; this was of direct assistance in selecting the incineration technology for experimental purposes and also lent supportive dialogue to the public relations program.

A complex management structure was employed for the Kepone incineration Test. Responsibilities for public information, technical evaluation of data, and development of a testing protocol were divided among a variety of individuals. Health and safety was always held in the fore of all research experiments and resulted in a completely safe experiment. A series of incineration experiments was conducted where increasing concentrations of Kepone were mixed with sewage sludge and exposed to partial pyrolytic conditions in a rotary kiln followed by high temperature fume incineration and finally caustic scrubbing with the calculated combustion efficiency always in excess of 99.99 percent.

INTRODUCTION

In the aftermath of the severe environmental contamination and the employee medical problems associated with the production of the pesticide Kepone in Hopewell, Virginia, the cry was heard loud and clear for a concerted effort to safely dispose of the Kepone and Kepone contaminated materials. Several task forces were established to review and assess the problem. The Administrator of the U.S. Environmental Protection Agency established a Kepone Task Force at the Federal level and the Governor of Virginia established a Task Force at the state level. The overall charge of both was to assess the problem, determine the best available short-term disposal options available and to determine the long-term environmental problems associated with Kepone contamination in the aquatic food chain. The later charge will take longer to determine and will have many economic and social overtones to it before Kepone is completely removed from the environment.

With the aforementioned goals in mind, the U.S. EPA, Office of Research and Development, and Solid and Hazardous Waste Research Division undertook a laboratory research study to develop thermal degradation data for Kepone and related pesticides.(1) Meanwhile, the Virginia Task Force, through their contractor Design Partnership, was evaluating disposal alternatives and planning for the ultimate disposal of all Kepone and Kepone contaminated materials.(2) After evaluating existing disposal options, laboratory data supported the hypothesis that under controlled combustion conditions Kepone could be safely destroyed. Design Partnership recommended that thermal destruction was the safest, most economical, and most convenient method of disposal of these materials.

Historically, extrapolating laboratory results to full scale operations has not been generally successful. Therefore, the recommendation was made to conduct a pilot scale test burn using the information gained in the laboratory. In addition to confirming the lab results, the pilot scale study could also serve to define the range of operating parameters needed for safe disposal of Kepone. Because of the physical form of the material requiring disposal, it was agreed that the system for these pilot scale tests necessitated a rotary kiln which, in conjunction with a temperature above 1100°C, could volatize the material and yield a residence time greater than 2 seconds. In addition, the installation should have the necessary pollution control devices to remove the natural products of organochlorine incineration.

The research facilities of the Surface Combustion Division of the Midland-Ross Corporation in Toledo, Ohio had the required hardware to conduct the pilot scale testing, and were subsequently selected for this study.

THE KEPONE INCINERATION TEST (KIT)(3)

While making the necessary arrangements for the KIT it became apparent that this particular program required a public information program, a well planned and supervised health and safety program, and a technical group to plan, coordinate and evaluate the KIT results. After much discussion, the overall program management structure presented in Figure 1 evolved, which offered the strongest possible control over the program by both the responsible governmental bodies and by the technical staff assigned to the project. The plan was for the detailed experiments to be carried out under the direction of the Experimental Management Group, implementing stringent safety procedures established and monitored by the Health and Safety Group. A committee of representatives from the various Federal, state, and local agencies whose responsibilities included air and water quality control was organized and designated the Burn Authority (BA). The results of each experiment were presented to the Burn Authority who had at least one representative on site at all times. The BA

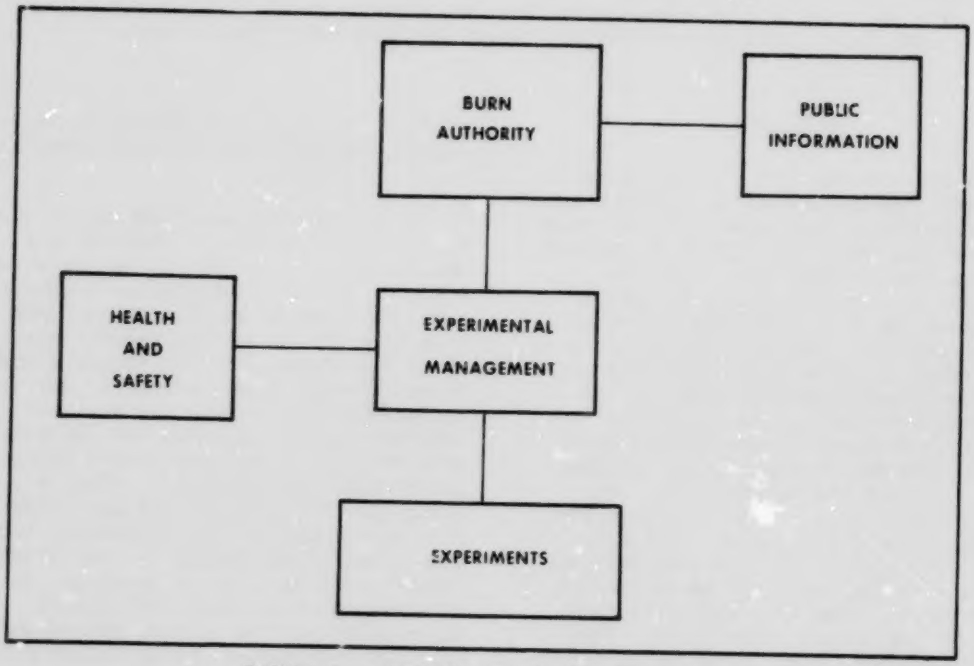

FIGURE 1. PROGRAM MANAGEMENT STRUCTURE

reviewed results of each test, and was empowered to decide whether the program should proceed as scheduled, or be modified. The results of each experiment and the BA decision were then transmitted to the public through the Public Information Group.

In spite of the obvious complexity of the management structure just discussed, it worked quite successfully. The dedication of the BA members to their responsibilities to the public and their sympathy for the stated goals and objectives of the program, were in no small way responsible for the successful outcome.

EXPERIMENTAL

A schematic of the physical layout for the experiments conducted at the Surface Combustion Division is shown in Figure 2. Main components and their characteristics are discussed below:

1. Rotary kiln pyrolyzer. The rotary kiln pyrolyzer, 1.52 m in diameter and 3.0 m in length, was fitted with rotary seal charge and discharge connections so as to minimize the leakage of gases into or out of the kiln. The kiln was heated with one 500,000 Btu/hr gas burner calculated to maintain a nominal temperature of 500°C. The kiln, designed for batch feed, was modified for the KIT such that sludge mixed with Kepone could be Moyno pumped into the kiln at a nominal rate of 45 kg/hr (100 lb/hr).

2. Fume Incinerator/Afterburner. The fume incinerator, with a residence chamber volume of 2.4 m^3, was fired by two

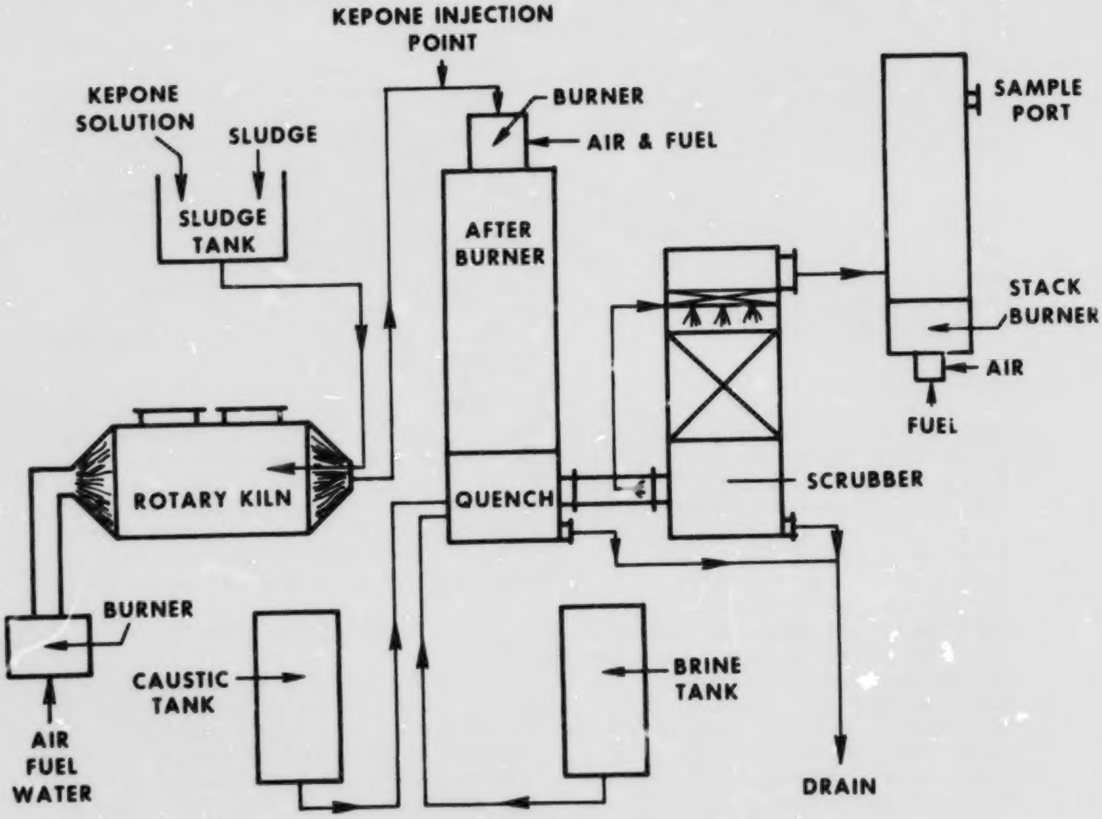
KEPONE INJECTION POINT
KEPONE SOLUTION
SLUDGE
SLUDGE TANK
BURNER
AIR & FUEL
AFTER BURNER
SAMPLE PORT
STACK BURNER
AIR
FUEL
ROTARY KILN
QUENCH
SCRUBBER
BURNER
CAUSTIC TANK
BRINE TANK
AIR
FUEL
WATER
DRAIN

FIGURE 2. KEPONE INCINERATION TEST SYSTEM

500,000 Btu/hr gas burners. The system was designed to operate at temperatures above 1100°C and still maintain a residence time for hot gases in excess of 2 seconds.

3. Quench. Cold water was injected into the bottom of the incinerator as a quench. This promoted evaporative cooling of the hot gases in the incinerator.

4. Scrubber. The scrubber, a tower 76 cm in diameter, was packed to a depth of 1.83 m with 5 mm Intalox plastic saddle packing. A liquid distributor at the top of the packed bed caused the liquid to be evenly distributed across the packed bed. The mist eliminator consisted of a 15 cm deep bed of saddles placed above the liquid distributor. The gas flow through the entire system was by an induced draft fan with a $0.94 m^3$/sec capacity mounted at the top of the scrubber. The pH of the scrubber water was monitored and continually adjusted with 12% caustic solution to lie between nine and ten.

5. Sludge Feed System. Kepone contaminated sludge was simulated by mechanically mixing in the feed tank the appropriate amounts of Kepone dissolved in acetic acid and Toledo sludge.

6. Direct Injection Feed System. The direct injection experiments were designed to study the feasibility of directly injecting Kepone containing low Btu fluids into the incinerator without passing through the kiln. These experiments, as well as those conducted with sludge, were planned so that in succeeding experiments the amount of Kepone could be increased or the specific set of operational variables could be altered. The direct injection experiments were terminated when the results indicated that another sequence would be likely to cause the 25 ng/m^3 ambient air standard imposed on this test to be violated.

The health and safety precautions for this research were well planned so that all operating personnel would have sufficient time and space to be isolated from Kepone contamination. The general outline of these procedures can be seen in Figure 3, where the operations and control area are shown in conjunction with the kiln and mixing areas.

The operations and control area, which included the incinerator, the scrubber, the furnace operational equipment, and the brine and caustic storage tanks, was enclosed by a wooden framework lined on the inside with heavy plastic. This area was accessible only to specifically authorized personnel through locked doors and was considered to be minimally contaminated. Operating personnel in the area were required to wear disposable coveralls, rubber boots, and rubber gloves. Upon leaving, it was required that hands and face be washed and protective clothing be stored in appropriate containers.

In the kiln and mixing areas much more detailed precautions were taken. These areas were most likely to be exposed to Kepone and its solutions, thus it was designated as hazardous. Personnel working in these areas were required to wear full protective gear, including a respirator. Further, when the operator was handling the acetic acid he was required to wear a face mask. The only entrance to this area was through the change and shower area; the doors shown to the outside from the mixing room were emergency doors (Fig. 3).

The change and shower area was provided to assure proper isolation of the facility. Contaminated clothing was kept within the change area and personnel exiting from the kiln and mixing areas had to shower before dressing in street clothes. Also, all personnel in the operating area were required to shower at the end of day.

EXPERIMENTAL RESULTS

The results of the experiments with Kepone incineration are presented in Table 1. As can be seen, the ambient air standard of 25 ng/m^3 for Kepone, set on an interim basis, was not violated in any of the experiments. In fact, most experiments have a combustion efficiency of at least 99.9999%. Such detailed calcula-

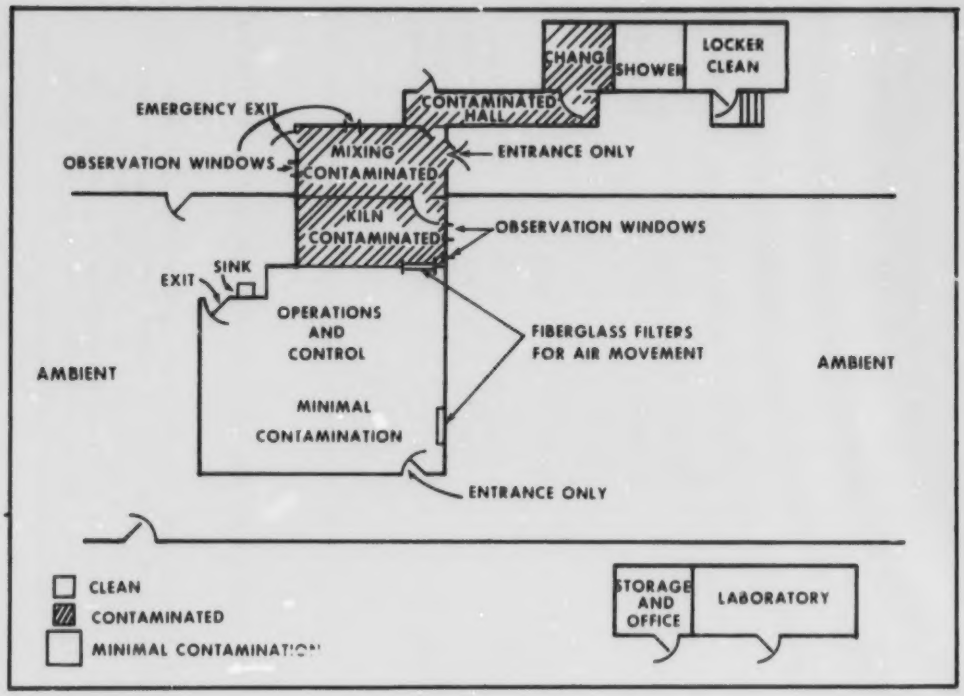
LOCKER CLEAN
SHOWER
CHANGE
CONTAMINATED HALL
EMERGENCY EXIT
OBSERVATION WINDOWS
MIXING CONTAMINATED
ENTRANCE ONLY
KILN CONTAMINATED
OBSERVATION WINDOWS
SINK
EXIT
OPERATIONS AND CONTROL
MINIMAL CONTAMINATION
FIBERGLASS FILTERS FOR AIR MOVEMENT
AMBIENT
AMBIENT
ENTRANCE ONLY
CLEAN
CONTAMINATED
MINIMAL CONTAMINATION
STORAGE AND OFFICE
LABORATORY

FIGURE 3. EXPERIMENTAL AREA--ISOLATION PLAN

tions were permitted by the extremely precise analytical support present during the KIT.

The continuous interaction of the Burn Authority with the Experimental Management Group was of great benefit to the overall program. This form of program management proved to be a viable and useful tool that should be considered in future efforts concerning hazardous materials that have received adverse publicity.

The stack was sampled using the EPA Standard Method Five with an RAC Stack-sampler®. After each sludge and stack sample run, samples were analyzed using accepted procedures. A number of Kepone standards were run as reference checks on retention times.

It was calculated that during the course of the KIT some 1000 individual analyses were performed at the site by one chemist and one technical assistant.

CONCLUSIONS

A summary of the results and conclusions derived from the KIT program are presented below:

1. Coincineration of Kepone with sewage sludge was a safe and environmentally acceptable method for disposing of Kepone. The results of these experiments indicated that the destruction efficiency for Kepone is greater than 99.9999% in a system consisting of a pyrolyzer and a fume incinerator which operates at temperatures above 1000°C and has a residence time of at least 2 seconds.
2. Direct injection of low Btu solutions of Kepone was not a useful process. This does not rule out the possibility of using a high Btu solution of Kepone and incinerating it.
3. Adequate safety instruction coupled with constant monitoring

TABLE 1: SUMMARY KEPONE INCINERATION EXPERIMENTS

Experiments	Kepone Feed Rate (gms/min)	Total Feed Time (min)	Total Kepone Fed (gms)	Stack Emission Concentration(1) (gm/m^3)	Total Stack Output (gms)	Afterburner Temp. (^oC)	Combustion Efficiency %
Injection runs							
1	acetic acid only	-	-	-	-	1260	-
2	1-67x10^{-5}	130	2.16x10^{-3}	ND	ND	1260	100(3)
3	1.67x10^{-5}	135	2.25x10^{-3}	ND	ND	1093	100
4	1.67x10^{-5}	100	1.67	ND(2)	ND(1)	1093	100
5	1.50	115	172.5	5.35x10^{-8}	1.76x10^{-4}	1093	99.99991
Sludge runs							
6	Toledo sludge only	120	-	ND	ND	1093	-
7	5.68	315	1789	1.7x10^{-8}	1.85x10^{-4}	1149	99.9999
8	5.68	240	1354	2.4x10^{-8}	1.85x10^{-4}	1093	99.9999
9	5.68	220	1241	2.55x10^{-8}	1.53x10^{-4}	1093	99.9999
10	24.2	165	3995	2.95x10^{-8}	1.67x10^{-4}	1093	99.9999
Totals			8553		1.58x10^{-3}		

(1) Measured at stuck conditions, not ambient conditions.

(2) Apparent Kepone peak on chromatogram of filter collected. The Kepone peak did not appear after base partitioning of original extract.

(3) To speak of 100 percent combustion efficiency is somewhat unrealistic but is a natural consequence of the definition for efficiency of combustion in those situations for which there is so small a stack load of Kepone that it was undetectable. Further, the expression of the combustion efficiency in terms of 6 or 7 decimal places is justified since even if both the input rate and the emission rate were in error by as much as 25 percent, the extremes would only effect the combustion efficiency in the sixth decimal place -- again a consequence of the definition of the combustion efficiency and the very small emission rates that were found.

to assure the proper use of safety equipment was necessary to prevent exposure of operating personnel.

4. The layout and the isolated location of the facility prevented the escape of Kepone into the surroundings, and at the same time made it easy to clean up after the tests were completed.

5. Real time analyses of Kepone on site was highly satisfactory and of great assistance in the decision making process.

6. The Burn Authority control led the KIT program very satisfactorily.

7. A completely informed public was an ally rather than an antagonist when experimenting with material that had previously received a large amount of adverse publicity.

Results of the KIT indicated that land-based incineration technology is available which will safely and adequately dispose of the presently stored Kepone and that of the sludge lagoon in Hopewell. The geometry of a full scale system would naturally not be the same as existed at the Surface Combustion Division. The KIT program was designed to determine the feasibility of incineration for the disposal of Kepone and to evaluate data generated from laboratory research. To this end, the KIT was a successful venture.

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The Development of a Leaching Test for Industrial Wastes

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ABSTRACT

Recent legislation dealing with land disposal of industrial or hazardous wastes has focused attention on potential water pollution resulting from such practices. This paper provides a summary of procedures as well as some of the background information and rationale which led to development of a laboratory test procedure to assess the leaching potential characteristics of a particular waste. The procedure results in information regarding the types of materials leached from a waste, an estimate of the maximum concentration likely to be observed of these materials, an estimate of the amount of each material likely to be released per unit weight of waste, and an indication of the effect of co-disposal with mixed municipal refuse or other specific wastes on the leaching potential of the waste being tested.

Introduction

Recently an increased awareness of the potential for ground water pollution from industrial wastes disposed in landfills has become evident. Since many wastes will not produce polluting leachates when landfilled, there is need for criteria to discriminate between wastes that will produce hazardous leachates and those that will not. One such criterion is a short standardized leaching test which subjects the waste in the laboratory to simulated landfill conditions or to test conditions that can be related to landfill conditions. The test would evaluate the leaching potential of the waste under landfill conditions by indicating what constituents would leach out of the waste, how much of that material would leach out and under what conditions they will leach. This paper summarizes a background study performed to develop such a leaching test. It will discuss the philosophy of leaching tests and the test variables affecting the leaching test, review some of the leaching tests that have been developed, and discuss briefly the procedure which evolved from this work and the interpretation of leaching test results.

Intensive vs. Quick Tests

Two general approaches can be used to evaluate the leachability of waste material: (1) a very intensive study of waste leaching characteristics, or (2) a quick test using standardized procedures. The intensive study gives more information about the leaching characteristics of a waste. Test conditions can be varied as needed, and the effects of different variables on the leaching characteristics can be studied. Such a test takes considerable time, money and personnel. The standardized test uses only predetermined testing conditions, and so cannot show the effects of the different variables of the waste leaching pattern. It can, however, give useful information in a short time which when properly interpreted can give an indication of the leaching characteristics of a waste. It is much cheaper, faster, and simpler than the intensive study.

Wastes generated in large quantities should be subjected to the intensive study, particularly wastes that are generated at different sites throughout the country but are of relatively uniform composition, e.g. fly ash or scrubber sludge. However, for the many wastes that are produced in relatively small amounts, a standard leaching test is more appropriate. The small amount of waste produced does not justify the expense involved in the intensive study unless the waste is of particular concern because of its characteristics or landfilling situation.

In an intensive test, factors affecting the test results will be varied and their effects observed and analyzed. In the standard test these factors will be set beforehand and their effects on the test results will not be observed. It is important to be aware of the test factors which are set in the standard test and their potential effect on the test results so that a proper interpretation can be made of the results.

Ideal and Practical Leaching Tests

Ideally a leaching test would determine four characteristics regarding the release of a parameter, A, from a waste:

1. the highest concentration of A to be found in the leachate;
2. the factors controlling this concentration,
3. the total amount of A available from a given amount of waste, and
4. the release pattern of A with time.

The last characteristic includes the kinetics of the release, physical or chemical changes occurring in the waste as it is leached, any effects of these changes on the release of A, and the influence of the waste on the leachate. Water quality standards are given in terms of concentration and since many toxic effects are concentration dependent as are most chemical reactions, concentration is of obvious interest. Maximum release is important when predicting the total amounts of A that may be leached from the waste in a landfill. It is also of importance when A may be accumulated, whether due to biological uptake or chemical processes (e.g. sorption onto soil, precipitation, etc.). Accumulated materials may be released at high concentrations if conditions change. With the four characteristics determined by the leaching test, the potential hazard of a waste can be evaluated, and the suitability of landfilling as a disposal technique assessed. The information from the test could also be used along with other information, to design waste processing or landfilling procedures so as to minimize the release of A from the waste.

A standard leaching test, as defined herein, will not give enough information to predict completely the four characteristics mentioned above; however, it will show the behavior of a waste under a prescribed set of conditions. These conditions can then be related to landfill conditions through modeling and careful selection of test conditions, and through correlation studies between test and actual landfill results. Correlation studies serve both to relate the non-modeled conditions to landfills and to verify the modeled conditions. With careful interpretation of results, an estimation of the behavior of a waste in a landfill can be made from standard test results.

Since the purpose of the test is to evaluate the leaching potential of a waste, it is reasonable to use an aggressive test to model a worst case situation. This is a conservative rationale. Further testing can then be done, if warranted, using conditions more typical of the long-term landfill situation.

A test which extracts only those components that would be leached in a landfill and extracts them in the same pattern that they would be extracted in a landfill is needed. A chemical solvent or series of solutions which would extract only leachable components would be ideal. Serial extraction procedures have been developed for soils and sediments; however, such procedures are based on a comprehensive understanding of the extraction process. This understanding requires that the chemical composition of the leached material and the chemical interactions between the material and the leaching solution be understood, and that the composition of the leached material be fairly consistent. Most of the wide array of landfilled wastes do not meet these criteria. The leaching test must then attempt to model landfill conditions, so the results are more readily related to full-scale landfill situations.

Batch and Column Tests

Two types of tests are commonly employed for determining the leaching potential of a landfilled waste—batch and column tests. In batch tests, a properly prepared sample of the waste to be tested is placed in a container along with leaching media. After a suitable period of time, and under conditions specified as being appropriate to the test, the elutriate or leachate is separated from the waste and analyzed to determine the material leached from the waste. Column tests, in which the waste is packed in a column and the leaching solution passed through, is a closer approximation of landfill conditions than a batch test, at least at first glance. The column test simulates both the waste—leachate contact (except around the column edge) and the rate of leachate migration found in landfills. The column test also is good for predicting the release pattern of A with time, since it models the continuous leaching and long time periods found in landfills. However, column tests have several disadvantages, such as the following:

1. problems arising from channeling and nonuniform packing,
2. potential unnatural clogging,
3. possibly unnatural biological effects,
4. edge effects,
5. long time requirements, and
6. difficulty in obtaining reproducible results even if done by experienced lab personnel.

All of these difficulties, but particularly the time requirements for an adequate column test (months to years), suggest that a batch test be chosen as the standard testing procedure. Both batch and column tests might be used in an intensive study.

Factors in a Batch Test

There are several factors affecting a parameter's concentration in the batch test elutriate which need to be considered in designing a leaching test. These factors are given in Table 1. Of particular interest in the development of a leaching test are the test conditions. These are discussed individually below.

A. Leachate Composition

Industrial wastes can be landfilled in one of three general categories of landfills as shown in Table 2. It is clear that the leaching media composition prior to waste contact is one of the key variables in a leaching test, and must be comparable to leaching media composition contacting the waste in the actual landfill for the test to have any practical significance.

For a monolandfill, distilled, deionized water or a synthetic rainwater can be used as a representative extractant or solvent. Alternatively, this landfill situation can be modeled by contacting the waste with a leachate produced by the waste itself. A sample can be contacted with leachate resulting from prior contact between another waste sample and distilled water, for example. This simulates what would occur if a drop of relatively uncontaminated rainwater passed through a thick layer of waste in a monolandfill.

Table 1

Factors Affecting Parameter Concentrations in a Batch Test

1. Sample treatment prior to test
    A. Sampling in industrial plant and shipment to test laboratory
    B. Sample treatment in laboratory prior to test
        1. subsampling procedure
        2. sample preparation (solid-liquid separation, drying, grinding, etc.)
2. Test conditions
    A. Leaching media composition
    B. Solid to liquid ratio
    C. Time per elution
    D. Number of elutions
    E. Temperature
    F. Agitation technique
    G. Surface area contact
3. Separation procedure and analysis after test

For co-disposal with mixed municipal refuse, both distilled deionized water and a municipal landfill leachate can be used. The water simulates rainwater and provides mild leaching conditions. A municipal landfill leachate has widely differing characteristics depending on the refuse composition and state of decomposition, dimensions of the landfill, age, degree of chanelling of moisture, and both long-term and instantaneous climatic effects, etc. Further, even for a given sample of such leachate, the composition is very complex, precluding developing an exact recipe from which leachate of both reproducible and realistic composition can be produced. Rather than attempt to define a standard landfill, from which leachates representative of different landfill ages would conceivably be obtained, it is more promising to examine the leaching characteristics of leachate typical of actively decomposing municipal landfills, and model a synthetic leachate on the results. Such a synthetic municipal landfill

Table 2

Classification of Landfills and Leachate Composition

Landfill Type	Waste Landfilled	Leachate Composition Controlled By
Monolandfill	By itself	The waste itself
Municipal	With municipal wastes	Municipal refuse decomposition products
Industrial	With other industrial wastes	Other industrial wastes

leachate has been developed as part of this study, which simulates aggressive leaching conditions which might be obtained by co-disposal of the waste being tested with municipal refuse.

The leachate produced in a heterogenous industrial landfill is the most difficult to model, since the material entering the landfill will likely vary in composition. In this case, two approaches may be used in the selection of leaching media. If the wastes in the landfill are known, a synthetic leachate can be developed based on characteristics of those wastes. Alternatively, a series of leaching solutions can be used, each emphasizing a single leaching parameter—i.e., acid base. complexer, organic solvent etc. Results obtained using different leaching solutions would indicate what types of wastes might be co-disposed with the waste in question. For example, a waste which released large amounts of an undesirable parameter under acidic leaching conditions should not be landfilled with acid or acid producing wastes.

The use of distilled water or other mild leaching solutions allows the waste to create its own leaching environment, whereas, a synthetic leachate or strong chemical solution essentially controls the leaching environment. For example, a waste containing small amounts of a leachable basic salt will raise the pH of a distilled water leachate, and only materials that are soluble in basic solutions will be found in the leachate. Conversely, use of a synthetic municipal leachate which is heavily buffered, or an acid leaching solution, will probably neutralize the basic salt while maintaining an acidic pH. In the first case the waste controls the pH of the solution, while in the second case the leaching media is the controlling factor.

B. Solid to Liquid Ratio

Solid to liquid ratios (or waste to eluent ratios) used in the test can have profound effects on test results. The concentration of a very soluble parameter will be directly dependent on the solid to liquid ratio (S/L). On the other hand, parameters for which concentrations are controlled by solubility will not show S/L ratio effects, but rather will have the same concentration at all S/L ratios, provided enough solid is present to saturate the system. S/L ratios can also affect concentration if adsorption or desorption processes are controlling the concentration.

In a given waste, several chemical constitutents may be of interest. These may have different factors controlling their concentrations, and so may show different dependencies on the S/L ratio. Several currently available leaching or elutriation tests start with high S/L ratios and saturated conditions, then decrease the ratio until unsaturated conditions are reached. This procedure could be complicated if more than one parameter of interest reached saturation at different S/L ratios.

The S/L ratio encountered by a drop of leachate percolating through a landfill will be very high, by the very nature of percolation. If there were extensive channeling in the landfill, however, this would not be true.

The choice of a solid/liquid ratio for use in the test is based on practical considerations. A very high S/L ratio, such as is used in the saturation test, is most likely to result in many components being saturated. This makes it difficult to estimate the total release of a component from the waste, since many elutions will be necessary to elute the leachable fraction of the component. Also, it is often difficult to obtain enough leachate for analysis with a high S/L ratio. On the other hand, a very low S/L ratio can produce very low concentrations of the parameters of interest, leading to analytical problems.

An interesting approach to the

selection of an S/L ratio is used in the State of Illinois E.P.A. test as reported in reference(1). The ratio to be used for a waste R is calculated from the equation $R = 5.34\ D$, using the waste density (D) for the wet waste and a constant based on the average annual rainfall in Illinois. Thus, the S/L ratio is based on volume rather than weight, and can be readily interpreted in terms of landfill conditions and annual rainfall. If the results of a leaching test are to be directly related to landfill conditions, a correlation between the annual rainfall, the waste density, and the test S/L ratio will need to be made in order to determine how much leachate a unit area of waste will contact per unit time, and thus the time span to which the S/L ratio used in the test corresponds. The Illinois test is interesting in that the correlation is determined before rather than after the test is performed.

C. Time per Elution

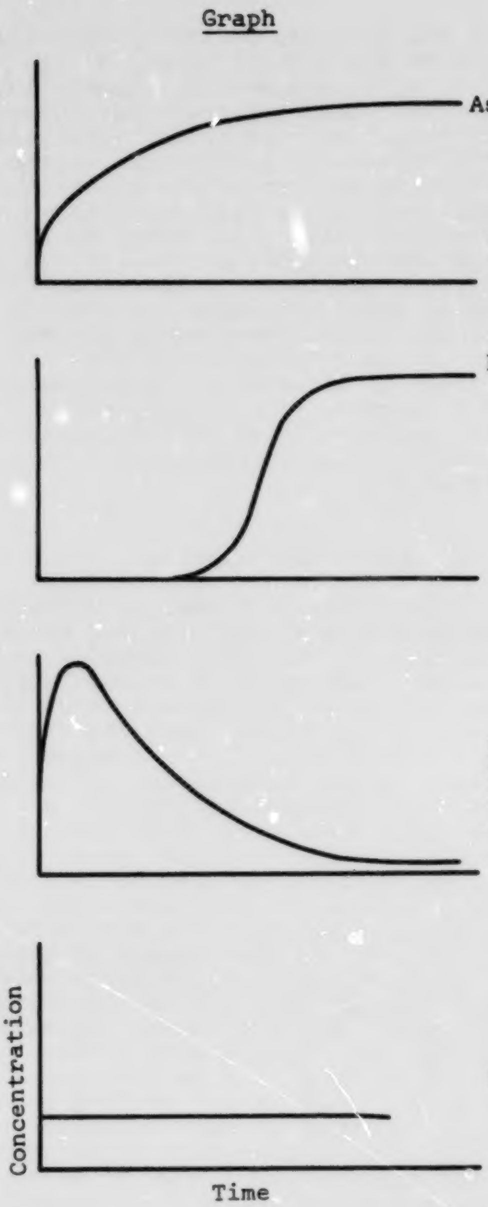
Ideally, either each elution would allow the parameter of interest to come to equilibrium, or it would be designed to study the release kinetics of the parameter. In practice both situations are difficult to obtain. Different paramaters may equilibrate at different rates. Lee and Plumb(2) found four release patterns in a leaching study using taconite tailings, as shown in Figure 1. The time span for their experiment was 500 days. The experiment used a very low S/L ratio (5 to 35 gm taconite per 10 liters distilled water), with periodic sampling. Not only did equilibration times for different parameters vary widely, but for some parameters a series of reactions occurred which produced concentration maxima with subsequent concentration decreases. The varieties of release patterns found make it apparent that no one sampling time could be chosen which is the best for each of the release patterns. Nor can a short leaching test be assumed to measure equilibrium concentrations of a parameter, or even to determine all the parameters that would be released from a waste. Of course, the four patterns found by Lee and Plumb are not the only release patterns possible; different wastes may have different and possibly unique release patterns.

The selection of an elution time is arbitrary. Some considerations do apply, however. The test should be long enough to allow rapidly equilibrating species to approach equilibrium and analytically determinable amount of most species to be released, yet short enough to minimize biological growth in the test chamber, secondary effects, and consistent saturation of species of interest. Biological growth can produce constantly changing conditions and could make test results very difficult to interpret. Consistent saturation of chemical species would require many elutions to be performed. Finally, the time chosen should be convenient to personnel, if possible.

By removing samples at various times during an elution, one obtains information about the release kinetics of a rapidly equilibrating specie. However, unless the contact time between the waste and leachate in the landfill are known, this information may be difficult to apply to a landfill situation. It could be used to determine the equilibrium concentration of a parameter. The additional work involved makes this determination more appropriate in an intensive test rather than a standard leaching test.

D. Number of Elutions

The information obtained from more than one elution often justifies the extra work involved. Successive elutions can indicate the release pattern of a parameter over time, and often can give an idea of the factors affecting the release of the parameter. Successive elutions are particularly important when the release of one parameter, A, is inhibited by the release of another parameter, B. For example, imagine a leaching situation with a



Type	Example
Asymptotic Release	Specific Conductance Alkalinity, Ca, Mg and others
Exponential Release	Silica (a slow hydrolysis step needed before Si is solubilized)
Release followed by loss from solution	Co,Zn - loss due to rising pH in solution or absorption back onto solids
No Release	Several species

Figure 1

Types of Release in Long-Term Leaching Test Mentioned by Lee and Plumb with Examples from their Leaching Experiment Using Talconite Tailings(2).

waste containing a soluble basic parameter (e.g.,a carbonate) and an acid soluble, base insoluble component (e.g., a trace metal), being leached by an acidic leachate. The carbonates in the waste will neutralize the acid leachate until the carbonates have been leached from the waste. Incoming acidic leachate will then reestablish acidic conditions and bring the trace metal into solution. If only one elution were used, or if the test were ended before the acidic pH had been reestablished, the potential for trace metal leaching would be completely overlooked. More than one elution can also sometimes indicate the factors controlling the release of a soluble parameter—steady concentrations over several elutions may indicate solubility or desorption control, whereas, a rapidly falling concentration indicates washout.

The additional information obtained from repeated leachings needs to be balanced against the extra work involved. The experience of the authors is that the most useful information is obtained in the first several leachings. One reasonable approach is to use a set number of elutions, say three to five, with more elutions suggested if an indicator parameter, e.g. pH, has not returned to a baseline value.

In the discussion above, it has been assumed that the same waste sample has been eluted several times with fresh leachate. An alternative approach is to use the same leachate sample to elute several fresh samples of waste. This procedure provides information regarding the maximum concentrations that a parameter can reach in the leachate, rather than indicating release characteristics. By using both elution techniques—replacing either the leaching media or the waste in subsequent elutions—one can obtain considerably more information about the waste than by using either procedure alone.

E. Temperature

Temperature should have an effect on the leaching pattern of a waste due to its effects on solubility and reaction kinetics. Generally, however, leaching tests have been conducted at room temperature, and the effects of temperature on the leaching pattern of a waste within the range of average laboratory temperatures may not be great enough to justify specially controlled temperature conditions. Temperature should be measured and reported, however. Occasionally, temperature control can be very important if the waste itself is affected by temperature. For example, if a solid component of the waste melts at room temperature, constant temperature conditions are important.

F. Agitation Technique

An agitation technique which promotes mixing without causing waste particle or container abrasion is needed. Agitation is needed to avoid concentration gradients between the leachate in contact with the waste and that at a distance; however, overly vigorous agitation can cause particle abrasion (Boyle, et. al.(3)) and give unnaturally high results. One agitation technique, used in some tests, involves shaking for a short time followed by settling. The authors found that this procedure results in the development of significant concentration gradients between the settled waste and the leaching solution, and thus is not aggressive enough for a good leaching test. Other methods, such as reciprocal shaking, wrist action shaking or circular shaking are more suitable provided they produce well-mixed systems and are slow enough so as to not promote abrasion.

G. Surface Area Contact Between Waste and Leachate

For some wastes, the amount of surface area in contact with the leaching solution can be important in controlling parameter concentrations in the leachate. For example, viscous liquid or solid wastes which are water-impervious but which contain water soluble parameters, can show this behavior. Such species can be leached from the surface of the waste, where they are in contact with the water, but not from the interior of the waste since the waste is impervious to water. Diffusion through the waste is generally too slow for these species to reach the surface.

If this situation is known to occur with a particular waste, the surface area of the waste in the test should be measured and the release calculated per unit surface area as well as per gram. Interpretation of this data, however, may be difficult unless it is known how the waste is going to be landfilled and whether physical breakdown of the waste occurs with time. The surface area of a waste may be controlled initially during sample preparation before the test by grinding, cutting, etc., or by the agitation technique.

Summary of Existing Tests

Several batch leaching tests have been developed. A survey of some of the existing tests has been done by the Mitre Corporation(1). A summary of the surveyed tests (plus two additional tests) is given in Table 3. The table provides both the range and the frequency at which values occur within the range for each of the various test variables discussed in this section. For those factors for which the selection of a value is somewhat arbitrary, as in the S/L ratio or the elution time, the range of values reported might be given consideration in the specification of values to be used in a test, and an average value (median or mode) used. For other factors (especially the number of elutions, for example), average values have little meaning. The wide variety in all the specified factors indicates the need for a standardized test so that results on different wastes and by different laboratories would be comparable.

A Standard Leaching Test

As part of a background study on leaching tests for the EPA, a standard leaching test has been developed by the authors (Ham, et. al.(4)). The test is summarized below.

The test utilizes only the solid portion of the waste being studied. The liquid portion, namely, that which will pass through a 0.45 micron filter, is analyzed directly for the components of interest. The rationale for the separation is that the liquid component of the waste can move away from the solid portion in the landfill, either due to gravity or capillary flow, or to absorption by surrounding materials. The liquid component of a waste represents an intrinsic potential impact on water quality as a result of waste disposal which is not dependent on external sources of water or leaching media. The solid portion remains behind for leaching, as simulated by the leaching test.

Two elution procedures are used in the test, as shown in Figure 2, one in which the waste is replaced in each elution (Procedure C) and one in which the leaching media or eluent is replaced (Procedure R). Procedure C is designed to estimate the maximum concentrations of leachable species arising in the leachate as a result of leaching media contact with the solid portion of a waste, while Procedure R estimates the amounts [illegible] leachable species to be released. The latter may be expressed with most wastes on a weight of each constituent released per unit weight of waste basis, for example. Both procedures use three 24-hour elutions with appropriate leaching media. The most common leaching media are likely to be distilled, deionized water and synthetic municipal landfill leachate, useful for modeling monolandfill and co-landfilling with mixed municipal refuse situations, respectively. If co-disposal with wastes which are not properly modeled by either of these leaching

Table 3

Summary of Existing Leaching Test Variables
(Number of Tests Specifying Each Operating Variable Indicated)

Leachates	No.
H_2O (dist, deion, dist-deion or unspecified)	17
H_2O with pH adjustment or simple acid or base	5
Site specific	1
Acetate buffer	1
Synthetic municipal landfill leachate	1
Synthetic natural rainwater	1
Bacterial nutrient media	1
Tests with more than one leachate	5

solid/ liquid ratio	range 1:1- 1:500	<1:4	1:4	1:5	1:10	>1:10	varied	calculated
		4	4	3	5	2	2	1
Time per elution	range 30 min -10 days	<1 hr	1-24 hrs	24 hr	48 hrs	72 hr	>72 hr	to "equil."
		1	3	7	3	2	3	2
No. of elutions	range 1-10	1	3	5	7	10		
		15	1	1	1	2		
Agitation	shaker, stirring & gas agitation used. Two tests use short agitation times with extended settling times.							
Surface area	Unspecified							

media is involved, appropriate media should be used. The most likely media in these situations would be of suitable controlled pH or a media obtained by distilled water contact with the other wastes involved.

For the first elution, both procedures use a 1:10 solid to liquid ratio (dry weight to volume). A separate sample of the waste is used to determine dry weight. In Procedure C, at the end of the first elution the sample is filtered and a portion of the leachate for analysis. Fresh waste is then added to the leachate. The amount of waste added is such that the solid to liquid ratio is 1:7.5 and 1:5 in the second and third elutions, respectively. The test is

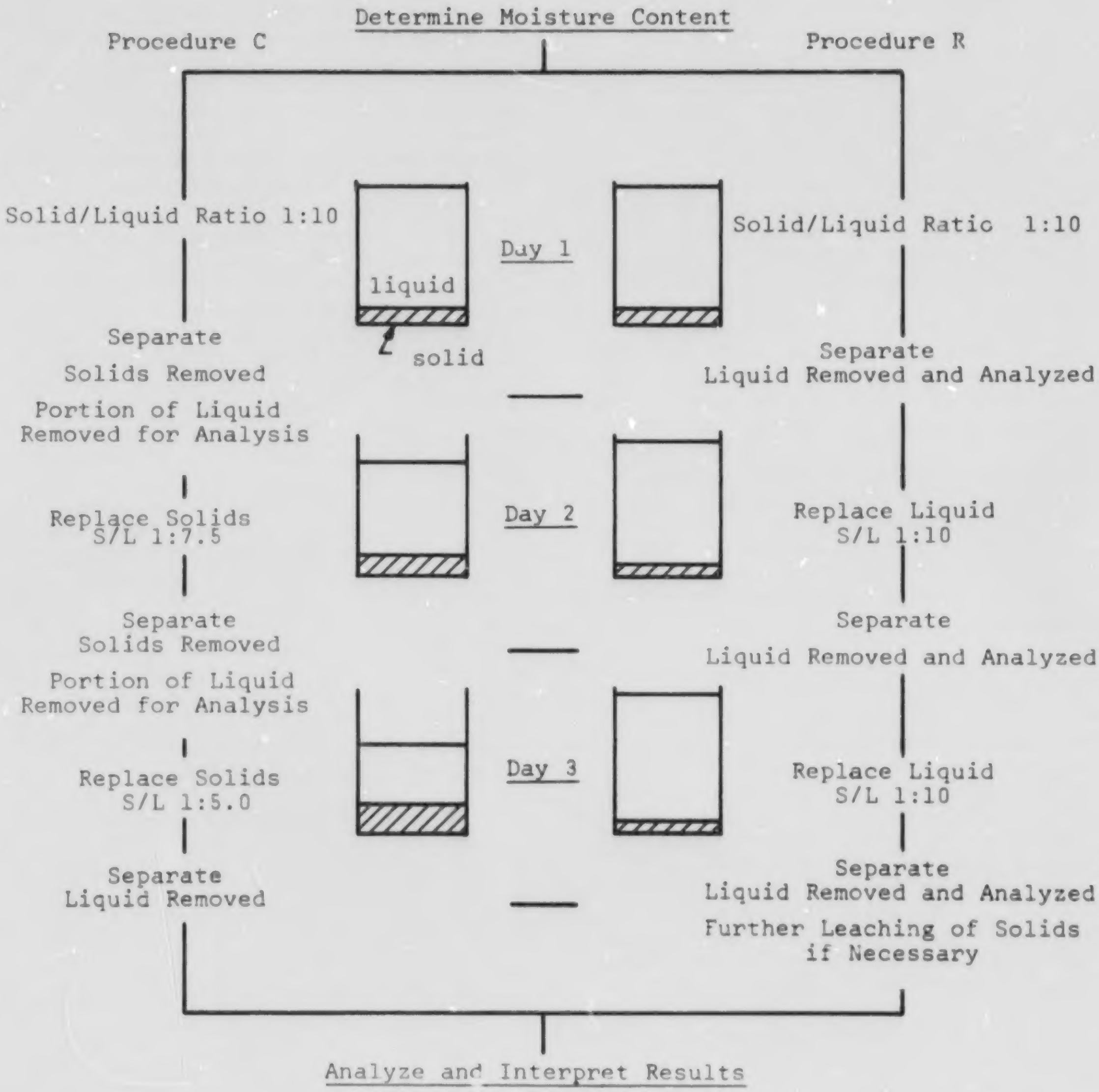

Determine Moisture Content
Procedure C
Procedure R
Solid/Liquid Ratio 1:10
Day 1
Solid/Liquid Ratio 1:10
liquid
solid
Separate
Solids Removed
Portion of Liquid
Removed for Analysis
Separate
Liquid Removed and Analyzed
Replace Solids
S/L 1:7.5
Day 2
Replace Liquid
S/L 1:10
Separate
Solids Removed
Portion of Liquid
Removed for Analysis
Separate
Liquid Removed and Analyzed
Replace Solids
S/L 1:5.0
Day 3
Replace Liquid
S/L 1:10
Separate
Liquid Removed
Separate
Liquid Removed and Analyzed
Further Leaching of Solids
if Necessary
Analyze and Interpret Results

Figure 2

Standard Leaching Test Flow Scheme

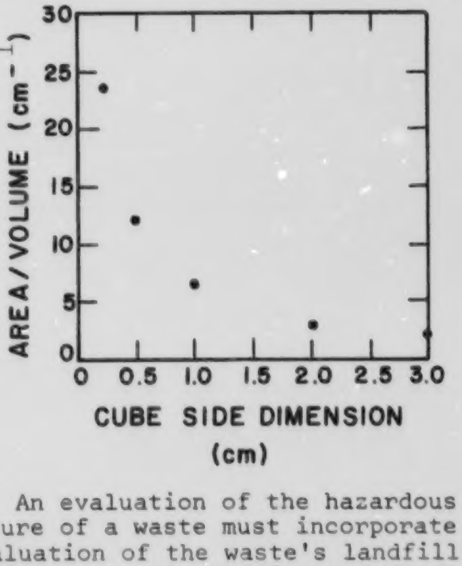
ended after the third elution. Procedure R uses fresh leachate on the same waste sample for each elution, thus maintaining a constant solid/liquid ratio of 1:10. More than three elutions may be used if there is a reason for the additional elutions (such as variable leachate composition after each successive elution). The test is run at ambient temperatures, unless special conditions dictate the use of a specific constant temperature. A rotating mixer is used in conjunction with a square sample bottle. The mixer is tilted to give an almost-vertical rotation plane. As the bottles turn, the samples slide down the square side and turn over somewhat in the process rather than simply staying at the bottom as would be the case in a round bottle. This shaking technique has been found to give good mixing with little or no abrasion. A 1 revolution per minute mixing speed is used. A more detailed description of the test and its development is given by Ham, et. al.(4).

Interpretation

Of the test conditions mentioned, leachate composition and temperature are most readily related to landfill conditions, as discussed previously. Other test conditions are more difficult to base on landfill conditions and are chosen based on criteria other than landfill modeling. Since these conditions can affect a parameter's concentration in the test leachate, caution must be exercised in data interpretation. One cannot always transpose test data to landfill practice directly. It may be possible to correlate test conditions with landfill concentrations by running extensive verification tests, correlating a waste's behavior in the test with the behavior of the same waste in a carefully monitored landfill. Correlation coefficients could then be developed for parameters and conditions similar to those in the verification study, and the test result used to estimate landfill concentrations.

A short leaching test cannot completely duplicate the long-term leaching characteristics of a waste. The short test might completely miss a parameter having exponential release (see Figure 1) or might overestimate the release of a parameter showing a concentration maxima. These patterns could be seen in a long-term study, but are difficult to determine in a short test.

When interpreting test results, it is important to consider the physical condition of the landfilled waste. Of special concern in this regard would be a waste which is landfilled in large stable chunks or with a stable impervious coating which could behave far differently in a landfill than in a test in which it were ground. Although not specifically tested as part of this study, it seems reasonable to cut, crush, or specially make such wastes to yield particles approximating the size equivalent to a 1 cm. cube, for example. This particle size is small enough to work in the procedure yet large enough to not increase drastically the surface area per unit weight waste exposed to leaching. This is observed by plotting the surface area per volume contained for cubes of varying dimension.



An evaluation of the hazardous nature of a waste must incorporate an evaluation of the waste's landfill environment. A waste's hazardous nature is a situation-specific characteristic. For example, a waste may be hazardous to an organism under one set of environmental conditions yet completely innocuous under a different set of conditions. Furthermore, its hazard may be organism specific, i.e., it may be hazardous to one organism and not to another under the same set of conditions. Thus a determination of the hazardous nature of a waste must include an evaluation of its effect on specific organisms (or plants or animals, etc.) under specific conditions.

One obvious way to interpret the leachate composition results is to compare the concentrations of the various chemical species to some standard, for example, drinking water standards. This is dangerous, however, and is difficult to defend for the leaching test developed in this study. Obviously, test requirements could have been adjusted to yield virtually any concentration of leachable species in the leachate for analysis. This could have been done, for example, by use of different elution times (e.g., 5 minutes instead of 24 hours), or solid/liquid ratios. The test was designed to be rapid, aggressive, and to yield as much information about the leaching characteristics of a waste as possible in a relatively short time. It was not designed to provide realistic concentrations of the various species for a specific situation.

One reasonable method for interpretation of test results involves adjustment of measured chemical specie concentrations by a factor. This factor may be based in part on the amount of leaching media the waste might contact during the estimated active life of the landfill. Thus, the cumulative infiltration expected over a ten-year period at an appropriate landfill might be used. This could be further modified by the amount of waste expected to be landfilled per unit landfill area. Another way of developing interpretive criteria would be to dilute both the leaching media and the elutriates obtained by waste contact to the point where no toxic effects are noted in a toxicity test. The difference in dilutions required to provide no toxic effects would be a measure of the incremental effect of the leachable constituents of a waste on the leaching media, and would thus be an indication of the hazardous character of the waste.

Once again the difference would have to be interpreted knowing that the test is designed to be aggressive, but at least the various base-level degrees of toxicity inherent in the selection of the raw leaching media are taken into account.

In summary, the standard test provides a rapid indication of which chemical species are immediately leached from a waste, and an indication of the maximum concentrations of each specie likely to be found in the leachate. In addition, an estimate of the amount of each specie likely to be released per unit weight of waste is obtained. Finally, the test can provide valuable information with regard to the relative effect of co-disposal of the waste in question with other wastes or mixed municipal refuse. The fact that the test is not perfect in predicting the long-term leaching pattern of a waste, or the precise concentration of a particular parameter in a particular landfill, for example, means that the test results need to be interpreted with care.

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GENETIC TOXICITY TESTING OF COMPLEX ENVIRONMENTAL EFFLUENTS

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ABSTRACT

We have used the Ames Salmonella histidine-reversion system and other genetic test systems to assay the mutagenic potential of crude synthetic oils and natural crude oils as exemplary complex mixtures. Extracts and leachates from particulate matter are also considered. Mutagenicity data on isolated or suspected organic components are presented. The results support the use of the short-term genetic tests in examining crude mixtures and point to the advantages of coupling the bioassays with chemical fractionation.

INTRODUCTION

The enormous amount of industrial and technological activity in the modern world creates a large number of chemical pollutants. The developing synthetic fuel industry is only one example that could have significant environmental impact on man. Although the health effects of chemicals in the environment are being extensively studied, it has become obvious that complex mixtures represent an unusual analytical problem.

Our work has emphasized test materials available from the developing synthetic fuel technologies(1). However, the procedures are applicable to a wide variety of industrial and natural products, environmental effluents, and body fluids. The general applicability of microbial test systems has already been demonstrated with, for example, the use of the assay as a prescreen for potential genetic hazards of complex environmental effluents or products, e.g., tobacco smoke condensates(2), soot from city air(3), fly ash(4), and, in our work with synthetic fuel technologies, oils and aqueous wastes(5-6). Other potential hazards arise from materials leached from raw materials, spent oil shales, ash/slag and other particulates.

In addition to obvious toxic effects, chemical pollutants may also produce carcinogenic, mutagenic, or teratogenic effects whose expression may be divorced in time from the actual exposure(s). The research effort described here specifically approaches the question of genetic hazard; but, as has been pointed out recently(7), certain microbial genetic assays (for example, the Ames test with Salmonella) show a high correlation between positive results in mutagenicity testing and the carcinogenicity of the compounds under test. The overall need to subject environmental chemicals to mutagenicity testing has been discussed in

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the Committee 17 Report on Environmental Mutagenic Hazards(8). Their key recommendation can be summarized as: "screening should be initiated as rapidly and as extensively as possible." DeSerres has discussed the utility of short-term tests for mutagenicity(9) and the prospect for their use in toxicological evaluation(10). He stresses that the data base of knowledge on untested environmental chemicals should be expanded, but cautions that "we are not ready, however, to extrapolate directly from data obtained in short-term tests for mutagenicity directly to man"(10). Tests on other organisms must be performed to validate and reinforce results from short-term tests. Short-term tests simply point out *potential* mutagenic and carcinogenic chemicals and serve to order priorities for further testing in higher organisms. Our approach has been to develop validating data in conjunction with ongoing analysis of synthetic fuels using *Salmonella*. Table 1 lists the assays currently being employed.

MATERIALS AND METHODS

The *Salmonella* tester series is composed of histidine mutants that revert after treatment with mutagens to the wild-type state (growth independent of histidine). Both missense mutants and frame-shift mutants comprise the set, and their reversion characteristics qualify the mechanism of action. In addition, the detection scheme yields the highest resolution possible by the inclusion of other mutations: (a) the deep rough mutation, *rfa*, which affects the lipopolysaccharide (LPS) coat, making the bacteria more permeable; (b) the deletion of the *uvrB* region, eliminating the excision-repair system(11), and (c) R factor plasmids, which increase sensitivity to mutagens.

Mutagenicity Testing. The *Salmonella typhimurium* strains used in the various assays are listed below. All strains were obtained through the courtesy of Dr. Bruce Ames, Berkeley, California.

TA1535 *hisG46*, *urvB*, *rfa* (missense)
TA100 *hisG46*, *uvrB*, *rfa* (missense plus R factor)
TA1537 *hisC3076*, *uvrB*, *rfa* (frameshift)
TA1538 *hisD3052*, *uvrB*, *rfa* (frameshift)

TABLE 1

SHORT-TERM BIOASSAYS

Test system	Assay
Salmonella	$his^- \rightarrow his^+$
E. coli	$arg^- \rightarrow arg^+$ $gal^- \rightarrow gal^+$
Yeast	$his^- \rightarrow his^+$ $CAN^s \rightarrow can^r$
Drosophila	Sex-linked recessive lethals
CHO cells	6-thioguanine resistance
Human leukocytes	chromatid aberrations
Mouse	dominant lethals
Carcinogenesis	skin painting

TA98 his D3052, uvrB, rfa (frameshift plus R factor)

In the routine screening of fractionated materials, the two strains TA98 and TA100 were generally used. Experimental procedures have been given by Ames et al.(11). The strain to be treated with the potential mutagen(s) is added to soft agar containing a low level of histidine and biotin along with varying amounts of the test substance. The suspension containing approximately 2 X 10^8 bacteria is overlaid on minimal agar plates, and revertants to wild type are counted after a 2-day incubation. The assay is quantitated with respect to dose (added amount) of test material and modified to include treatment with the liver homogenate required to metabolically activate many compounds.

Fractions and/or control compounds to be tested were suspended in dimethylsulfoxide (DMSO, supplied sterile, spectrophotometric grade from Schwarz/Mann) to concentrations in the range 10-20 mg/ml solids. The potential mutagen was in some cases assayed for general toxicity (bacterial survival) with strain TA1537. Generally, the fraction was tested with the plate assay over at least a 1,000-fold concentration range with the two tester strains TA98 and TA100. Revertant colonies were counted and plotted versus added concentration, and the slopes of the induction curves were determined. Positive or questionable results were retested with a narrower range of concentrations. All studies were carried out with parallel series of plates plus and minus the rat liver enzyme preparation(11) for metabolic activation. Routine controls demonstrating the sterility of samples, enzyme or rat liver S-9 preparations, and reagents were included. Positive controls with known mutagens were also studied in order to recheck strain response and enzyme preparations. All solvents used were nonmutagenic in the bacterial test system.

Samples. Exemplary oils that have been tested and their sources are listed below: (1) coal-liquefaction product from a process under development, courtesy of the Pittsburgh Energy Research Center (Synfuel A), or Coal A from ORNL repository; (2) a crude shale-oil sample (B) from the above-ground simulated in situ oil-shale retorting process; (3) Louisiana-Mississippi sweet crude oil, courtesy of Dr. J. A. Carter of the Analytical Chemistry Division, Oak Ridge National Laboratory.

The authors recognize the possibility that these samples may bear no relationship to the process as it may exist in the future, nor should it be construed that these materials are representative of all natural crudes, synthetic or shale-oil processes. They are used here simply as appropriate and available materials for the research.

Fractionation. The fractionation scheme described by Swain et al.(12), as modified by Bell et al.(13), has been applied to the product from the oil-shale process, Synfuel, and the natural crude. The separation scheme has been illustrated and detailed in reference 14. Reagent-grade solvents and glass-distilled water were used for extraction and chromatography.

RESULTS AND DISCUSSION

Chemical analyses of synthetic fuel materials(15-16) and predictions based on work with tobacco smoke condensates(12,17,18), give the investigator a general view of the organic components of the various fractions. Based on these predictions, we list a selected group (Table 2) of organic compounds pertinent to shale oil and synfuel, and the preliminary results on mutagenicity in the Salmonella histidine-reversion system. Although a number of the compounds may be promoters or modifiers of carcinogenesis (that is, active in co-carcinogenesis, perhaps in some cases as inhibitors), they do not appear to be mutagenic.

The major mutagenic components appear to be heterocyclic nitrogen compounds, aromatic amines, and polycyclic aromatic hydrocarbons.

In the investigation of the feasibility of the coupled analytical-mutagenicity assay approach, we fractionated the simulated in situ retorting shale-oil sample the synfuel sample, and the natural crude "control" oil sample into primary acidic, basic, and neutral components. Each primary fraction was then assayed with the Ames strains. Data are given for the frameshift strain TA98 with metabolic activation with enzyme preparations from

TABLE 2

MUTAGENICITY OF CHEMICALS KNOWN OR SUSPECTED TO OCCUR IN SYNFUELS USING SALMONELLA TESTER STRAINS

Chemical name	Strain	Mutagenicity
Acenaphthene	98, 100	+
Anthracene	98, 100	-
Benz[a]anthracene	100	+
Benz[a]anthracene,7,12-dimethyl	100	+
Benzo[a]fluorene	100	+
Benzo[a]pyrene	98	+
Chrysene	100	+
Fluoranthene	98	+
Naphthalene	98, 100	-
Phenanthrene	98	+
Pyrene	1537	+
Triphenylene	98	+
1,2,3,4-Dibenzanthracene	100	+
1,2,5,6-Dibenzanthracene	100	+
Acridine	1537	+
Carbazole	100	-
Isoquinoline	98, 100	-
Quinoline	98	+
7-Methylquinoline	100	+
8-Methylquinoline	100	+
2,6-Dimethylquinoline	98, 100	-
8-Hydroxyquinoline sulfate	100	+
8-Nitroquinoline	100	-
8-Aminoquinoline	1537	+
α-Naphthylamine	100	+
2-Acetamido fluorene	98	+

Aroclor 1254-induced rats (Table 3). The shale-oil and natural crude samples both contain significant activity in the neutral fractions and appear to represent comparable mutagenic hazards. However, the shale-oil material appears to contain additional activity in other fractions, particularly the B_E ether-soluble fraction. Synfuel is qualitatively similar to shale oil, although the B_{Ia} fraction is the most active encountered from these samples.

In addition to these exemplary samples, we have been applying the mutagenicity assay to a large group of synthetic fuel applications (Table 4).

The results presented here show that biological testing-within the limits of the specific system used-can be carried out with complex organic materials but perhaps only when coupled with the appropriate analytical separation schemes. The pri-

TABLE 3

MUTAGENICITY OF OIL FRACTIONS IN *SALMONELLA*[*]

Fraction	Natural Crude	Synfuel	Shale oil
$NaOH_I$	-	++	+
WA_I	-	+	+
WA_S	-	-	+
SA_I	-	-	-
SA_E	+	+	+
SA_W	+	+	+
B_{Ia}	-	+++	+
B_{Ib}	-	+	+
B_E	+	++	++
B_W	-	+	-
Neutral	++	++	++

[*] Revertants with frame-shift strain TA98.

- denotes no response over background.

+ denotes approximately 100 colonies over background.

++ denotes approximately 1000 colonies over background (at most effective volume added).

+++ denotes greater than 1000 colonies over background.

mary use that such combined chemical and biological work may serve is to aid in isolating and identifying the specific classes or components involved.

In these initial feasibility studies, the purpose has not been to reflect on whether a relative biohazard exists in comparison with other materials or processes. We feel an extrapolation to relative biohazard at this point would be, at least, premature. A number of precautions are listed below.

A number of biological discrepancies can enter into the determinations. For example, the short term assays chronically show negative results with, e.g., heavy metals and certain classes of organics. Similarly, compounds involved in or requiring co-carcinogenic phenomena would presumably go undetected. Concomitant bacterial toxicity can nullify any genetic damage assay that might be carried out; the choice of inducer for the liver enzymes involved can be wrong for selected compounds; and additionally, the applicability of the generally used *Salmonella* test to other genetic assays and the validation of the apparent correlation between mutagenicity and carcinogenicity still remains a point of significant fundamental research.

TABLE 4

OIL SAMPLES FOR MUTAGENICITY TESTING

Control	Coal liquifaction
Louisiana-Mississippi Sweet	Synfuel A (PERC)
Natural Crude Mix	Synfuel B (COED) Separator liquor
	Hydrocarbonization Process Hydrocarbonization liquid waste
	SRC Process
Shale Oil	Coal Gasification
Shale Oil*	Gasifier Condensates (PERC)
Product Water	Low BTU Gasification Ash, Tar, Particulates
Raw Shale Aqueous Spent Shale Extract**	

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*_In situ_ retort.

**Above ground retort.

The chemical integrity of the sample may be compromised. The choice of samples, their solubility, and the time and method of storage are unavoidable variables which may alter the composition of a sample. The detection or perhaps the generation of mutagenic activity may well be a function of the chemical fractionation scheme utilized. The inability to recover specific chemical classes or the formation of artifacts by the treatment could well corrupt the results obtained in addition to the possibility of an inability to detect the specific biological endpoint chosen.

In light of the difficulties pointed out above, we feel that over-interpretation of biohazard potential, i.e., rankings of relative hazard or reliance on negative results, should be approached with caution. However, in the context of a prescreen to aid the investigators in ordering their priorities, the short-term testing appears to be a valid testing approach with complex mixtures. Our experience to date with a variety of comparative assays (Table 5)(19) supports the contention that short term testing can be a useful predictor of potential genetic hazard in higher systems.

TABLE 5

COMPARATIVE MUTAGENESIS OF FRACTIONS FROM SYNTHETIC CRUDE OILS[a]

Test system	Assay	Basic fraction	Neutral fraction	Crude synfuel[b]
Salmonella	$his^- \rightarrow his^+$	+	+	+
E. coli	$arg^- \rightarrow arg^+$	+	+	NT
	$gal^- \rightarrow gal^+$	+	+	NT
Yeast	$his^- \rightarrow his^+$	+	+	NT
	$CAN^s \rightarrow can^r$	+	+	NT
Drosophila	SLRL	+	-	NT
CHO cells	6-thioguanine resistance	+	NT	NT
Human leukocytes	chromatid aberrations	P	+?	NT
Mouse	dominant lethals	-	P	+
Carcinogenesis	skin painting[c]	P	P	P

[a] The fractions utilized were generally those from Synfuel A-3, or Synfuel B-2. + = mutagenic; - = nonmutagenic; NT = not tested; and P = in progress.

[b] Crude synfuels are generally too toxic to test in most systems.

[c] Work of J. M. Holland, Oak Ridge National Laboratory, in progress.

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A FRAMEWORK FOR ECONOMIC ANALYSIS OF HAZARDOUS WASTE MANAGEMENT ALTERNATIVES

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ABSTRACT

This paper describes a methodology for analysing the economic and social effects of alternative approaches to hazardous waste management. The procedure involves the generation of a series of environmental 'threat scenarios' that might arise from the use of different hazardous waste management techniques, and identification of the 'parties-at-interest' to these techniques. By considering the likely attitudes of these parties-at-interest, a decision-maker can take into account social impacts as well as direct economic costs of alternative approaches to hazardous waste control.

INTRODUCTION

The purpose of this paper is to introduce some concepts and techniques that have been developed as part of an ongoing EPA-sponsored study.(1) A primary objective was to develop a methodology for the economic analysis of hazardous waste management problems. This methodology provides an analytical framework designed to assist a decision-maker to identify costs and other impacts associated with a given approach to hazardous waste management.

The general approach adopted is that of cost-risk-benefit analysis, but the methodology discussed here departs from the traditional approach in two ways. Rather than developing expected values for environmental damages, it concentrates on identifying and characterizing the threats to man and the environment which may arise from the use of various hazardous waste management techniques. Secondly, from the effects identified for these management techniques, it identifies 'parties-at-interest' and endeavors to predict ways in which these parties may respond. Their responses will, in turn, influence the outcomes from the use of alternative approaches to hazardous waste management.

The methodology is in the form of a general framework that is adaptable to specific situations. It is intended to help a decision-maker consider both the economic and social aspects of hazardous waste managementalternatives. It also permits evaluation of the effects of whatever degree of risk aversion is favored.

UNIQUE ASPECTS OF HAZARDOUS WASTE MANAGEMENT

As a first step towards developing a methodology for the analysis of hazardous waste management alternatives, an economist may ask the question "what is special about hazardous wastes, i.e., how does the economics of the management of these wastes differ from that of other wastes or pollutants?" A clear-cut answer to this question is difficult to find, but a definition of hazardous waste provides some indications of their special characteristics. A waste is hazardous if it

> . . . poses a substantial present or potential hazard to human health or living organisms because such wastes are lethal, nondegradable or persistent in nature or because they can be biologically magnified, or may otherwise cause or tend to cause detrimental cumulative effects [emphasis added]. (2)

Several distinguishing characteristics relevant to economic analysis emerge from this definition. First, *a hazardous waste can pose a substantial threat to man or the environment,* suggesting that hazardous wastes need more careful management than inert wastes or conventional pollutants (e.g., B.O.D.). Consequently, a management approach often used for conventional pollutants, that of permitting discharges that can be assimilated by the environment, may not be acceptable for hazardous wastes.

Secondly, *hazardous waste management will be more concerned with 'threats' or risks, as opposed to readily anticipated environmental impacts.* If, for example, a paper mill discharges an organic waste to a river, for some distance below the discharge point the level of dissolved oxygen in the water will fall. We have a reasonably good idea of what may happen to the aquatic life in this zone, and are relying on natural biological processes to 'treat' the waste and render it harmless, providing some local environmental degradation is acceptable. On the other hand, if a heavy metal waste is injected into a saline aquifer as a means of disposal, the intention is that the waste remains in the aquifer and thereby causes no harm to the environment. One must, however, be concerned about *threats* that may arise from the use of this disposal method. The saline aquifer may, for example, be interconnected with an aquifer used as a source of fresh water, which thereby becomes contaminated. Unlike the comparatively predictable effects from non-hazardous waste management techniques, it is usually difficult to estimate the probability that a threat will materialize, and the magnitude or cost of the potential damage may also be hard to predict.

Thirdly, *hazardous wastes are often persistent or non-degradable.* This is significant because (i) effects may be irreversible, and (ii) time scales of interest can be intergenerational. Injecting a heavy metal waste into an aquifer may be irreversible. (3) Should the aquifer later be needed as a water or mineral resource, or be found to be interconnected with a fresh water source, decontamination might not be feasible. Irreversibility can also introduce 'option value' and associated concepts that relate to the benefits of keeping options available. Thus, it may be desirable to delay making an irreversible decision until improved information is available (e.g., on the toxicity of a waste proposed for discharge); or changing values may mean that an irreversible decision made today is a regretted decision in the future.(4)

When today's decisions affect future generations, it raises the difficult problem of whether or not discounting is appropriate. The National Academy of Sciences pointed up this difficulty as follows:

> There have been long standing debates as to the appropriateness of applying a discount rate to effects on future generations, since any positive rate of discount will directly discriminate in favor of choices that involve bad impacts on

> later generations but not on earlier ones. . . . if the discount rate were 5 percent, 100 cases of toxic poisoning 75 years from now would be equivalent to about 3 cases today; or 1 case today would be valued the same as 1,730 cases occurring in 200 years . . . . Clearly, intergenerational effects of these magnitudes are ethically unacceptable. . . . Some other method of ethically weighting intergenerational incidence of effects must be devised. . . . there is no generally accepted method to weight intergenerational incidence of benefits and costs. (5)

Fourthly, hazardous wastes include those that are *biologically magnified* or have *cumulative effects*. These factors compound the difficulties of estimating damages due to exposure. It should, however, be noted that this problem is not unique to hazardous waste, as pollutants that are not normally regarded as hazardous may also have cumulative effects.

A final characteristic of hazardous wastes (one that is not apparent from the definition), is that *the composition of wastes can vary substantially,* not only because of different sources, but also from day to day for a given source. This complicates treatment to reduce the hazard and can inhibit resource recovery activities. Furthermore, it may mean that the degree of hazard posed by the waste is not well defined. (6)

To summarize, hazardous wastes are characterized by strong potential adverse effects, and their management may involve irreversible decisions and intergenerational time scales. Because insufficient information is available, the threats that these wastes pose to man and the environment are often difficult to precisely specify. Waste composition variability, magnification and cumulative effects compound the problem.

APPLICATIONS OF COST-RISK-BENEFIT ANALYSIS

Techniques of cost-benefit and risk-benefit analysis are well developed, and have already been applied to several classes of environmental problems*. For example, cost-benefit analysis has been applied to air and water pollution control programs, (10) while cost-risk-benefit (or risk-benefit) analysis has been used to compare alternative means of generating electric power (11).

Cost-benefit analysis is usually used to determine whether or not a project or an activity should be undertaken. Such analysis frequently involves determining the optimum scale of activity; i.e., the project scope at which the net benefit (total benefits less total costs) is maximized. Analysis of this type could be appropriate to deciding whether or not to create a park or to preserve a natural environment as a wilderness area.

Where we are dealing with pollution control, the economic activity that generates the pollutant is already in existence. Hence analysis considers only costs associated with pollution, and the conventional economic approach to pollution control becomes that of determining the optimum level of pollution, and devising a policy that results in that level. Conceptually (but not in practice) this is straightforward, and involves controlling the discharge of the pollutant to the level which minimizes the total cost, i.e., Q1 in Figure 1.

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*The distinction between cost-benefit and risk-benefit analyses is not usually clear-cut. The term risk-benefit analysis is often applied to a category of cost-benefit analysis in which risks to life and health are an important component of the costs. (7) It would not be applied to an analysis in which the risks are purely economic (e.g., where there is construction cost uncertainty, or where there is doubt about the magnitude of the project benefits). Some authors dealing with risks to life retain the term cost-benefit analysis (8), while others use the term cost-risk-benefit analysis to suggest that the costs include both conventional costs and risk-related ones (9).

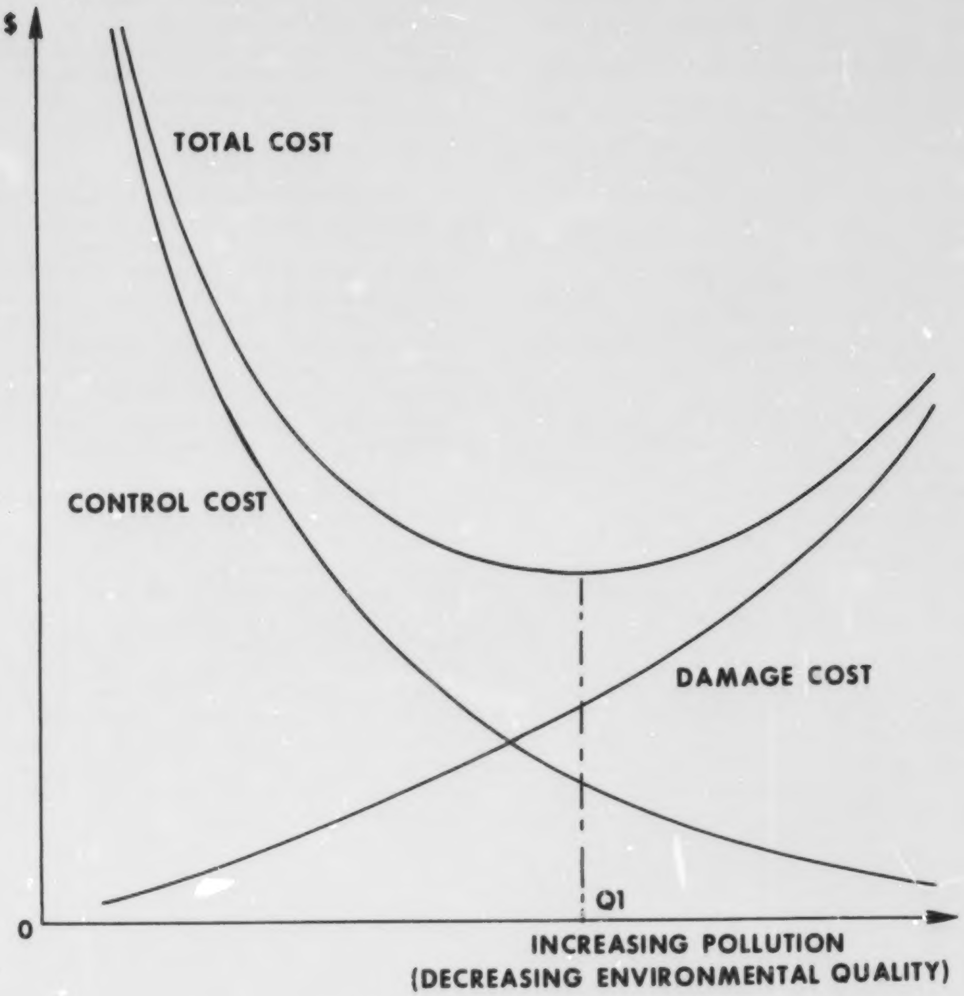

FIGURE 1. CONVENTIONAL APPROACH TO POLLUTION CONTROL

Cost-risk-benefit analysis can examine whether or not an activity that involves risk should be undertaken or permitted. It could, for example, be used to decide whether or not a particular toxic substance should be manufactured. Alternatively, the net benefit of the activity may be assumed to be positive, and the analysis used to compare different ways of achieving the objective. Thus, in assessing alternative means of generating electric power the expected numbers of mining and transportation accidents, etc. have been estimated and expressed as a cost; but the need for power has not been questioned. (12,13)

A feature of many cost-risk-benefit assessments is that they use expected values to describe the risks. By assigning economic values to the risks, an expected value of total cost can be obtained, and the least cost means of achieving the specified objective determined. Alternatively, the expected value approach can allow the optimum level of exposure to risk (e.g., radiation exposure from mammography (14)) to be determined in a manner that is analogous to Figure 1. This is possible where risks are statistically well defined; but the approach takes no account of a decision-maker's risk aversion, which may be the critical factor in policy decisions.

Hazardous wastes are highly diverse, and the threats that they pose to man and the environment can vary considerably with the circumstances. This makes it difficult to accurately define the probability that a threat will materialize, and to estimate the magnitudes of associated damages. The conventional economic approach to pollution control (Figure 1) implies a single pollutant or some index of pollution as the independent variable. Construction of an index representing the magnitude of threat would be complex. In any event, for most problems data requirements would be enormous. The methodology suggested here is intended to overcome these difficulties.

DESCRIPTION OF THE METHODOLOGY

The aspects of the methodology described here are those related to the use of threat scenarios and the social interaction process.

THREAT SCENARIOS

Assessing the damages caused by pollution is almost invariably more difficult than determining control costs. According to Fisher and Peterson, there are four stages in the assessment of damages from conventional pollution sources (15), as shown in the upper part of Figure 2. Starting with a specified emission or waste discharge, the ambient conditions and the physical effects must be determined before the dollar damage costs can be estimated. To extend Fisher and Peterson's model to hazardous wastes it is necessary to add a preliminary stage; identification of the possible threat mechanisms. One could then model the effects of the threats and arrive at dollar costs associated with each threat.

The central concept of the methodology presented here is to replace the first three stages (emissions, ambient conditions and effects) of Fisher and Peterson's damage model by a 'threat scenario' as illustrated in the lower part of Figure 2. The threat scenario would describe what might typically happen when a specified threat became a reality. More than one scenario could be used to depict different outcomes from a given threat mechanism. While qualitative descriptions are useful, where possible quantitative data should be used, based on modelling studies or judg-

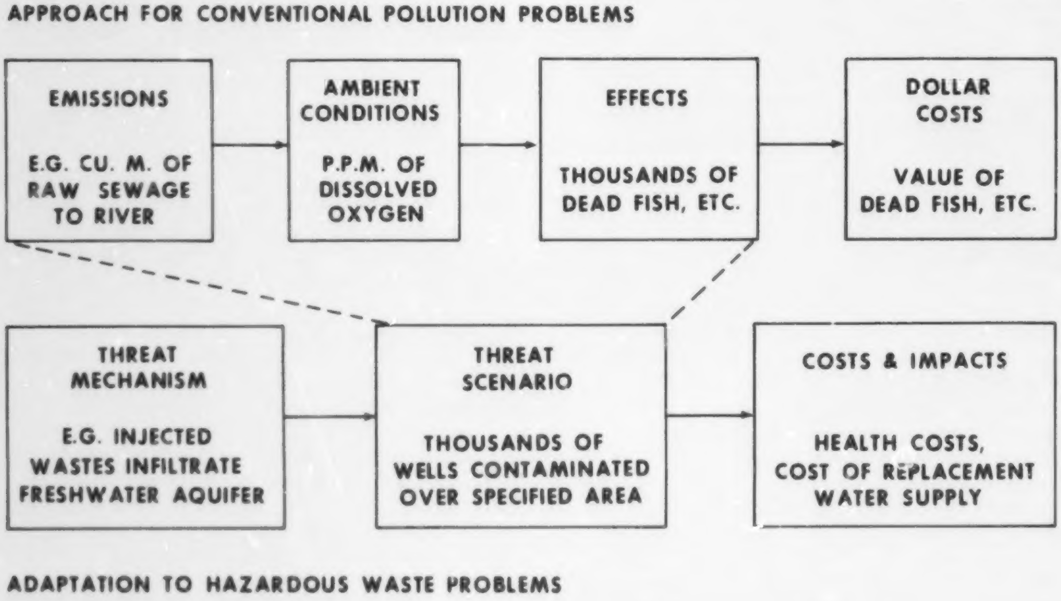
APPROACH FOR CONVENTIONAL POLLUTION PROBLEMS
EMISSIONS
E.G. CU. M. OF RAW SEWAGE TO RIVER
AMBIENT CONDITIONS
P.P.M. OF DISSOLVED OXYGEN
EFFECTS
THOUSANDS OF DEAD FISH, ETC.
DOLLAR COSTS
VALUE OF DEAD FISH, ETC.
THREAT MECHANISM
E.G. INJECTED WASTES INFILTRATE FRESHWATER AQUIFER
THREAT SCENARIO
THOUSANDS OF WELLS CONTAMINATED OVER SPECIFIED AREA
COSTS & IMPACTS
HEALTH COSTS, COST OF REPLACEMENT WATER SUPPLY
ADAPTATION TO HAZARDOUS WASTE PROBLEMS

FIGURE 2. DAMAGES ASSOCIATED WITH HAZARDOUS WASTE MANAGEMENT

ments reflecting actual experience with that type of threat.

A major difficulty with threat scenarios that are not based on adequate data, will be to choose a scenario in which the magnitudes of the effects are appropriate to the types and quantities of wastes concerned, and to the local circumstances (e.g., geohydrologic conditions). In some situations, worst case assumptions could be used to place upper limits on effects. In evaluating the effect of landfill leaching, for example, it could be assumed that after many years a 'steady state' is reached in which the leachate contains the same quantities of non-degradable toxic elements as enter the landfill, and that this leachate enters the local river system without attenuation. Given the streamflow, the average concentration of toxic elements in the river can be calculated, and the effect on aquatic life predicted.

Clearly numerical estimates that do not adequately reflect local conditions are unlikely to be accurate. We are, however, interested in individuals' reactions to the threats from hazardous waste management alternatives. These reactions may reflect past experience with a similar threat mechanism under different circumstances. (16) Responses to threats depend on perceived magnitudes and probabilities, which may be at variance with reality. Hence, the mere identification of threats is an important part of the methodology, even if the magnitudes of their impacts and the probabilities of their occurence are not well defined.

Each threat scenario provides a largely physical description of what may happen from the use of a given hazardous waste management technique. In principle, each scenario can be translated into economic terms using established techniques for valuing the effects. (17,18) In practice, however, it can be difficult to attribute dollar values to some types of environmental impact. Additionally, there may be major uncertainty about the magnitude of these impacts. Hence, in the lower part of Figure 2, the term costs and impacts has been used for the final stage (i.e., the output) of the threat scenario approach. This refers to dollar costs where determinable, and to descriptions of social impacts where dollar costs cannot realistically be assigned.

IDENTIFICATION OF THREATS

A key step in analyzing alternatives is to identify environmental threats associated with each control technique. Figure 3 presents a morphological map that demonstrates in a general way how a threat evolves from some initiating event to some physical outcome. (19) Although the map is not fully detailed, it can be seen that there are numerous ways in which threats could develop. It will be necessary to limit the threats considered in analysis to those believed to be comparatively probable, based on previous experience or consensus judgment taking local conditions into account. Table 1 lists the major techniques that are available for hazardous waste management, and identifies some of the more important threats that may arise from the use of each technique.

There is some published information on the environmental threats that may arise from hazardous wastes. Lazar, et al., have analyzed the mechanisms involved in over 400 'incidents' (i.e., threats that have materialized) arising from the disposal of hazardous waste to land. (20) Ground and surface water pollution have been by far the most common outcomes of inadequate disposal methods, followed by contact poisoning. The EPA has published detailed descriptions of some of these incidents (21-27), while other sources contain additional data on damage from leachates and injected wastes. (28,29)

Data on transportation accidents are widely available, and some statistics on in-plant accidents have been developed. (30) Dawson and Stradley have published data on the probabilities and sizes of spills of hazardous chemicals, and have also determined the probability that these spills will reach surface waters. (31) Fish kill reports collected and published by the EPA provide a useful indication of the impacts on surface waters from spills and dumping. (32)

There have recently been a number of attempts to estimate the probability and effects of some infrequent or gradual geologic and climatic events (e.g., earthquake, erosion, tornado) that might affect the disposal of high level radioactive wastes. (33-35) Schneider and Platt even include a tentative estimate of the probability that an aquifer will develop where

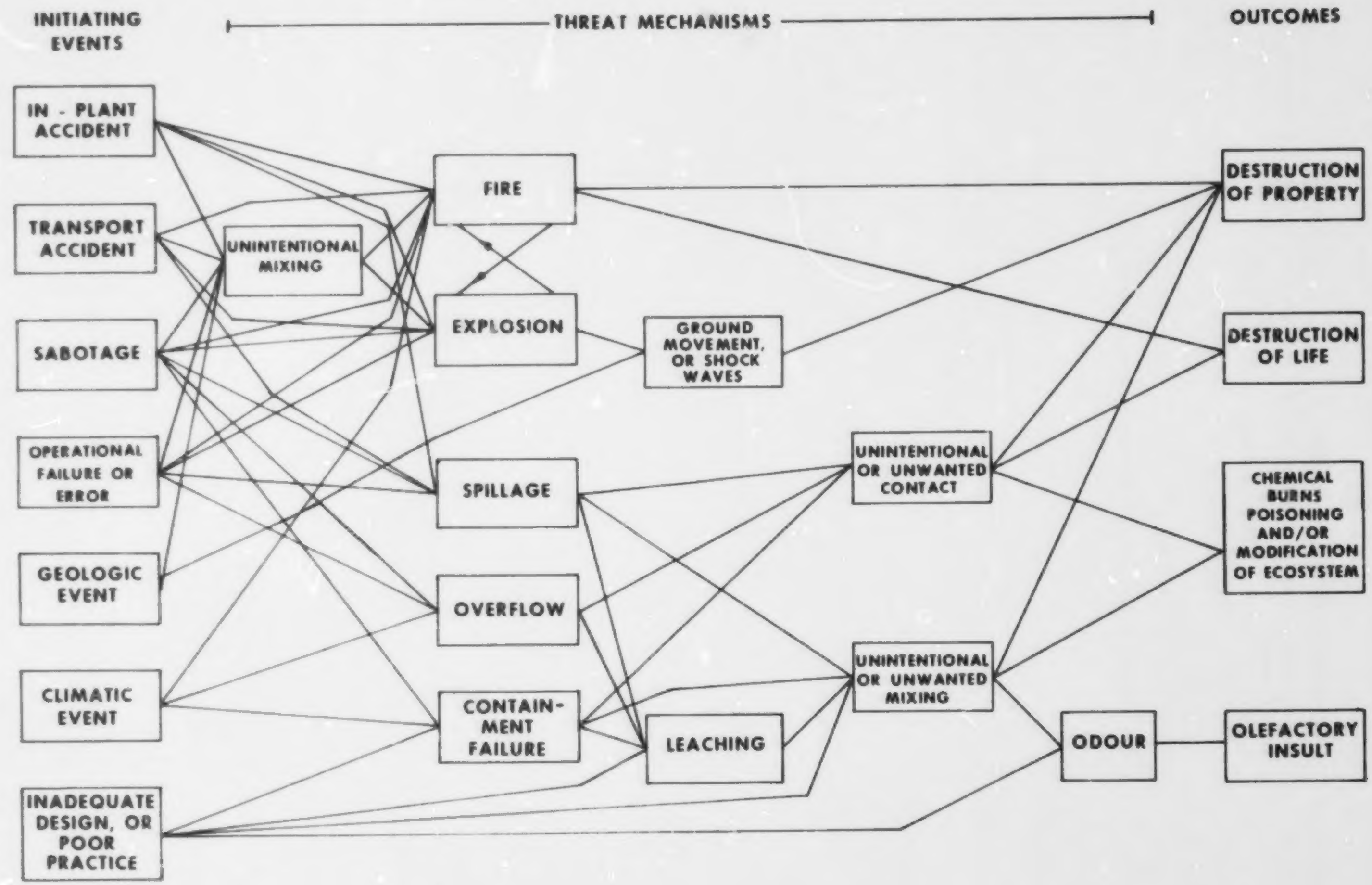
INITIATING EVENTS
THREAT MECHANISMS
OUTCOMES
IN - PLANT ACCIDENT
TRANSPORT ACCIDENT
SABOTAGE
OPERATIONAL FAILURE OR ERROR
GEOLOGIC EVENT
CLIMATIC EVENT
INADEQUATE DESIGN, OR POOR PRACTICE
UNINTENTIONAL MIXING
FIRE
EXPLOSION
SPILLAGE
OVERFLOW
CONTAIN-MENT FAILURE
GROUND MOVEMENT, OR SHOCK WAVES
LEACHING
UNINTENTIONAL OR UNWANTED CONTACT
UNINTENTIONAL OR UNWANTED MIXING
ODOUR
DESTRUCTION OF PROPERTY
DESTRUCTION OF LIFE
CHEMICAL BURNS POISONING AND/OR MODIFICATION OF ECOSYSTEM
OLEFACTORY INSULT

FIGURE 3. MORPHOLOGICAL MAP OF ENVIRONMENTAL THREATS

TABLE 1. HAZARDOUS WASTE MANAGEMENT TECHNIQUES AND ASSOCIATED THREATS

TECHNIQUES	MAJOR ENVIRONMENTAL THREATS	COMMENTS
All techniques	Surreptitious dumping to land, sewer or waterway Accidental fire/explosion/spillage leading to damage/destruction of property and life (all forms) Water contamination Chronic poisoning (workers)	Threats can occur at generating or treatment plants, also during transport
	The threats below are in addition to those listed above	
Change in waste streams		
-process change		To generate wastes that are less hazardous
-source reduction		To generate less of hazardous waste
-waste separation		To separate hazardous waste from non-hazardous waste
Resource recovery		
-materials recovery		
-energy recovery		
Treatment to reduce hazard	Treatment may fail leaving waste still hazardous	Failure most likely with biological treatment
-physical		Physical and chemical treatment may facilitate resource recovery
-chemical		
-biological		
-thermal	Air pollution	
-encapsulation		To immobilize wastes
Land application	Crop take-up of toxic elements Soil sterilization Leaching/run-off Odor	
Landfilling	Leaching/run-off Odor	Vector could also be a threat
Mine disposal	Leakage to groundwater	
Lagooning (for storage or evaporation)	Seepage to groundwater Overflow Odor and air pollution	
Deep well injection	Contamination of usable groundwater Land movement and (consequent) property damage	Some modification of groundwater system is inevitable
Ocean dumping	Modification of marine ecosystem	Threat is inevitable but extent difficult to predict
Engineered storage	Containment failure	Failure poses same threat as All Techniques-accidents
Space disposal	Contamination of space	Threat largely unknown
Discharge to sewer	Waste may destroy biological treatment colonies Waste may cause sewage sludge to become hazardous "Slugs" of waste may overload system	Not hazardous waste management techniques, but included because they may be involved accidentally or surreptitiously
Discharge to waterway	Waste may destroy aquatic life	

none currently exists, and that it will penetrate a mine disposal site. (36)

THE INTERACTION PROCESS

Figure 4 presents the authors' schematic model of the interaction process involved in hazardous waste management decision-making. This model is central to the methodology and demonstrates all the essential elements used in the analytical framework, as described below. *Policy objectives* are considered to be an exogenous input to the analysis.

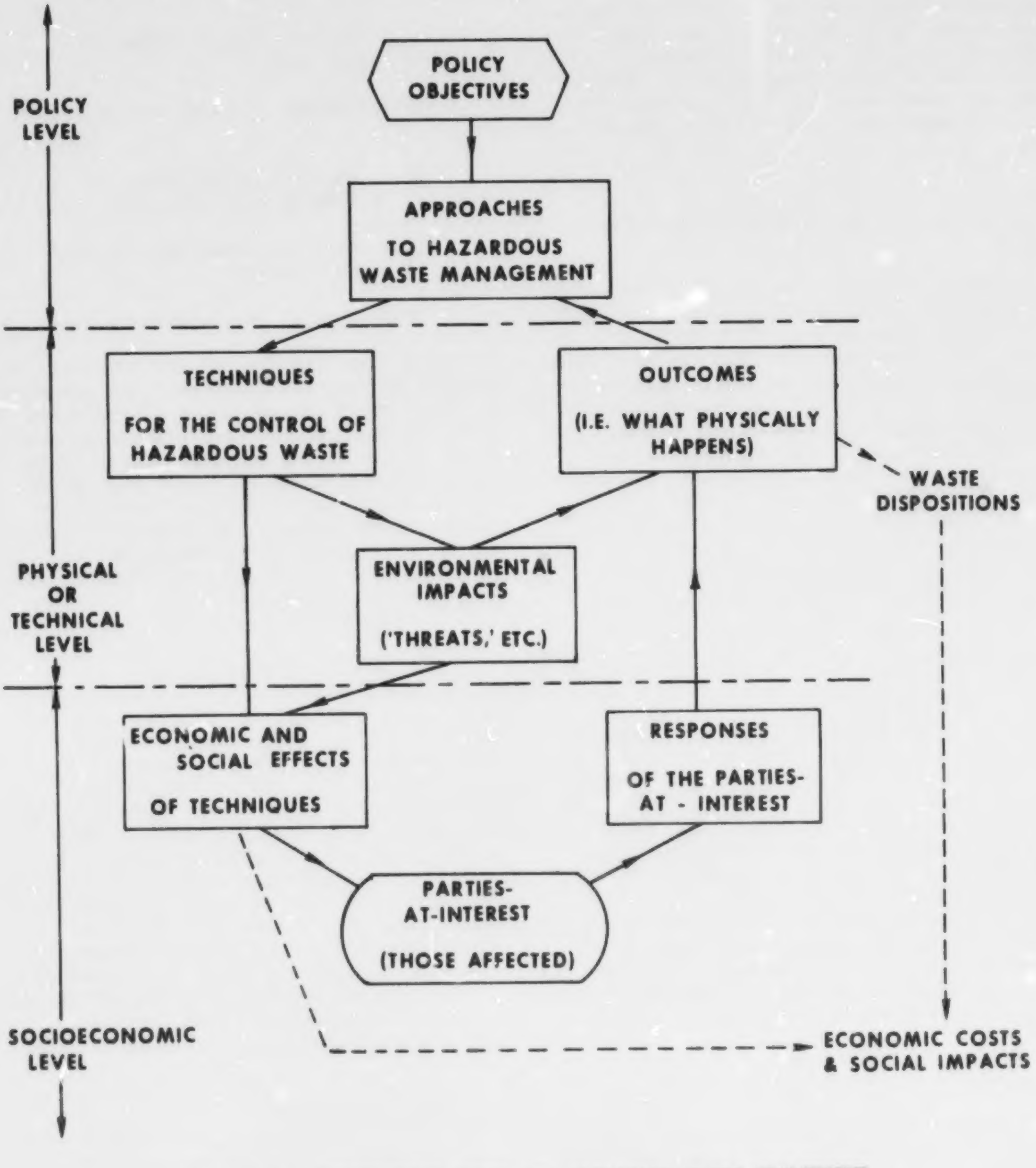
POLICY LEVEL
POLICY OBJECTIVES
APPROACHES TO HAZARDOUS WASTE MANAGEMENT
TECHNIQUES FOR THE CONTROL OF HAZARDOUS WASTE
OUTCOMES (I.E. WHAT PHYSICALLY HAPPENS)
WASTE DISPOSITIONS
PHYSICAL OR TECHNICAL LEVEL
ENVIRONMENTAL IMPACTS ('THREATS,' ETC.)
ECONOMIC AND SOCIAL EFFECTS OF TECHNIQUES
RESPONSES OF THE PARTIES-AT-INTEREST
PARTIES-AT-INTEREST (THOSE AFFECTED)
SOCIOECONOMIC LEVEL
ECONOMIC COSTS & SOCIAL IMPACTS

FIGURE 4. INTERACTION MODEL FOR HAZARDOUS WASTE MANAGEMENT

Approaches to hazardous waste management

Each *approach* to hazardous waste management represents a general concept or actual strategy consistent with the policy objectives to be attained. Approaches can be quite specific, such as requiring landfill disposal of all hazardous wastes, or prohibiting ocean dumping. Alternatively approaches can endeavor to *influence* waste management by providing economic incentives for desirable techniques or disincentives for those considered undesirable. Examples include tax-breaks for resource recovery, or effluent charges on certain disposal techniques.

Techniques for the control of hazardous waste

From the approaches to hazardous waste management, it is possible to predict which control techniques are likely to be used in practice. The term *technique* refers to the physical methods that may be used to eliminate or reduce hazardous waste generation, to treat wastes, or to dispose of them (refer to Table 1). The linkages between approaches and techniques may not be clear-cut, and the approaches are likely to change and be developed as the analysis progresses. Therefore a wide range of techniques should be considered in the early stages of analysis.

Environmental impacts

The next step is to determine the *environmental impacts*. The major impacts associated with each technique will be threats. These can range from the very unlikely (e.g., earthquake destruction) to virtual certainties. In general, emphasis should be placed on identifying and characterizing the impacts of the more probable threats associated with each technique. If, however, a relatively unlikely threat poses disastrous consequences, this should also be considered. Resource consumption (e.g., energy, land use) may also be a significant environmental impact.

Economic and social effects

The effects of the techniques on man are shown as *economic and social effects* in Figure 4. These effects may be both direct and indirect (primarily via threats). Direct effects include the waste generator's disposal costs, program administration costs and other costs including subsidies given to encourage preferred waste management techniques.

The major effects that can arise via environmental threats are listed below.

(i) Destruction or damage to man-made structures.

(ii) Damage to human life and health.

(iii) Destruction or damage to animals, vegetation and land ecosystems.

(iv) Fish and other aquatic life kills in surface waters.

(v) Changes in property values.

The first four effects can inflict costs on various parties ranging from those actually incurred (e.g., clean-up and repair costs) to those that reflect aesthetic considerations. Loss of option value (for example, not preserving an aquifer that may represent a useful resource in the future) is another form of cost. In principle there are ways to attach an *economic cost* to each of these effects, but in practice some will defy quantification, and may be listed as *social impacts* (see Figure 4).

Changes in property values are interesting because they provide a measure of the external effects of pollution. (37) They may reflect changes in consumers' utility due to the physical presence of pollution, or they may be completely psychological, reflecting concern that some sort of incident may occur (e.g., that a landfill may pollute a property owner's well). The preceeding example illustrates that *it is the way in which individuals perceive a threat that will determine their behavior*. Thus, a threat does not have to actually materialize, or even have a significant probability of occurence, in order to be important to an individual, and analysis should take account of this.

Parties-at-interest

In order to conduct analysis that recognizes differing viewpoints, it is useful to identify *parties-at-interest.* Each party-at-interest consitutes a class or group of individuals or firms that have a common interest and viewpoint on the outcome of any particular hazardous waste management alternative. For analysis, the parties-at-interest must be limited to those that are significantly affected by one or more of the alternatives. Gilmore, et al., who developed this concept, list four categories of parties-at-interest, as follows:

- Parties internal to the affected industry: e.g., owners, stockholders, management, employees and their unions.
- Suppliers and customers of an affected industry: e.g., vendors of materials and of services including financing, insurance and advertising, intermediate and final consumers. A more comprehensive listing may be available from an input-output analysis.
- Government: e.g., at different levels, and in different roles. Includes legislator, executor, adjudicator, taxer, regulator, and keeper of economic stability, social welfare, and national security.
- Affected bystanders: e.g., resources, wildlife, recreation potential, those concerned with aesthetic effects, and those secondarily involved such as investors, employees, residents, and other property owners. (38)

Table 2 presents a matrix of the parties-at-interest for each major technique, and suggests the nature of the effect that use of the technique has on each party-at-interest. It may be useful to examine a few of the entries in Table 2 to understand how the authors' judgments about the nature of the effects were made. Consider, for example, a technique involving chemical treatment to reduce hazard potential. Management of the firm generating the waste may have mixed views about this (+ -); it is likely to be comparatively costly, but treatment should reduce the risk of an adverse incident. The firm's workers are likely to favor treatment (+) because it probably makes their jobs safer. The effect on the waste disposal and transport industries will depend on the process streams following treatment (+ -); they may have safer wastes to dispose of (+), or there may be no waste requiring off-site disposal (-). Local officials are likely to favor chemical treatment due to the reduced risk of an environmental incident (+), but water supply authorities might be concerned over the possible discharge of an undesirable effluent to a river that constitutes part of a water supply (-). While water supply authorities and environmentalists are likely to have definite views on most techniques, the perception of threats and benefits from chemical treatment may be remote to most local residents (no entry in Table 2). Thermal treatment, on the other hand, could cause the deterioration of local air quality and might be viewed negatively by many residents and property owners (-), while a technique such as lagooning could pose a definite threat to local water supply users (-).

Responses of the parties-at-interest

The parties-at-interest will oppose or seek to mitigate effects perceived as being adverse, but will accept favorable effects, although they may be less likely to behave aggressively. Parties-at-interest may respond in ways that have direct economic consequences; for example, waste generating firms will seek to pass some or all increased operating costs on to their customers, while residents adversely affected by air pollution might move to another location.

Outcomes

The physical *outcomes* of a specific approach to hazardous waste management follow from the responses of the parties-at-interest and will include environmental impacts that actually occur, as well as the disposition of the wastes. Outcomes could include such effects as reduced sales of products resulting from higher prices, changes in property values, etc.

The outcomes provide feedback to the approaches to hazardous waste management. A decision-maker can examine the outcomes and associated economic costs and social

TABLE 2. MATRIX OF EFFECTS ON THE PARTIES-AT-INTEREST

Key:	Nature of effect
++	Very favorable
+	Generally favorable
+-	Mixed, or depends on circumstances
-	Generally adverse
--	Very adverse
	Not significant

Party-At-Interest

Hazardous Waste Control Technique	Waste generators-management	Waste generators-workers	Competing firms (different process)	Waste disposal industry	Waste transporters	Secondary materials industry	Local political officials	Local environmental officials	Local residents and workers	Local property owners	Water supply auth rities	Local water supply users	Fishermen (freshwater and ocean)	Recreation related industry	Environmentalists	Scientists	Other	Other Parties-at-Interest
Change in waste stream	+-	+-	+-	+-	+-	+	+	+			+-				+			
Resource recovery	+-	+-	+-	-	+-	++	+	+			+				++		-	Virgin material suppliers
Treatment - physical	+-	+	+-	+-	+-	+	+	+			+-		+-		+			
- chemical	+-	+	+-	+-	+-	+	+	+			+-		+-		+		+	Chemical suppliers
- biological	-	+-	+-	-	-	-	+-	+-			-		-		+-			
- thermal	+-	+-	+	-	-	-	+-	+-	-	-	+				+-			
- encapsulation	-	+	+	+	++	-	+	++			+				++			
Land application	+	+	+-	+-	+	-	-	+-	-	-	-	-	-		-		+-	Farmers
Landfill - secure	+-	+	++	++	++	-	+	+	-		+	+-			+			
- ordinary	+	+-	-	+	+-	-	-	-	--	-	-	-	-		-			
Mine disposal	-	+	++	++	++	+-	++	++			+				++		-	Adjacent mineral interests
Lagooning	+-	+-	-	-	--	-	-	-	--	-	-	-	-		--		-	Fowl hunters, farmers
Deep well injection	+	+	-	+-	+-	--	-	--		-	-	-			-	-		
Ocean dumping	+	+	-	++	+	-	-	--	-	-	+		--	-	--	--	-	Other nations, politicians
Engineered storage	-	+	+	+	-	+-	+-	+-	-		+	+-			+-			
Space disposal	--	+	+	+-	+	-	-	-			++				--	-	-	Other nations, politicians
Discharge to sewer	+	+	-	--	--	-	-	-			-				-		--	Sewer authorities
Discharge to waterway	++	+	--	--	--	-	--	--	-	-	--	-	--	-	--	-	--	Other water recreationists

impacts for each approach, and can then modify an approach, or select a new approach that appears to be more desirable.

OTHER ASPECTS OF THE METHODOLOGY

It is beyond the scope of this paper to fully detail the methodology; however, a few additional specific features will be mentioned.

Equity

Equity is a normative facet of economics, and identification of various parties-at-interest is particularly useful for considering the equity of an approach. By examining the way in which costs and impacts fall on different parties-at-interest, the decision-maker can evaluate the acceptability of the results. He can also devise strategies to render a given approach more equitable by finding ways to shift some of the costs and impacts between parties-at-interest. Examination of the alternatives for the disposal of a particular waste might, for example, lead to the conclusion that economic efficiency would be served by discharging this waste to a landfill, but that this would render the water in a limited number of wells unsafe to drink. To make this solution more equitable, arrangements could be made whereby the waste generator pays for the cost of installing and operating an alternative water supply. An additional payment could be made to compensate the well owners for a loss of psychic value caused by changing their water supply to an alternative source.

Intertemporal considerations

As already indicated, there is some doubt as to the appropriateness of discounting where irreversible decisions are involved that have effects over intergenerational time spans. This problem has recently been addressed in contexts other than waste management, and that work suggests that the appropriate solution may depend on the nature of any altruism that the present generation extends towards later generations. (39-41) On the other hand, discounting is almost universally used by industry and is accepted by economists where decisions are reversible or have a duration that is limited to one generation.

A possible practical solution to this dilemma would be to discount effects that occur during the first generation (i.e., a normal project life of two or three decades) but not to further discount any effect that occurs or extends beyond this time. (42) This suggestion is particularly attractive for use with this methodology as it eliminates some of the problems associated with the timing of threats. In most cases it is difficult to predict the time at which a threat will materialize if it does. Uncertainty may arise because the initiating event is random, because effects are cumulative and involve threshold levels, or simply because the data required to predict the timing are not available. If effects that occur after one generation are all discounted by the same amount, prediction of their timing becomes unimportant.

Unfortunately, it is possible only to use lump sum valuations of effects (e.g., a one-time clean-up or replacement cost for the effect of a threat) if the period of evaluation is infinite. Any annual cost (such as an option value or the cost of perpetual care) continuing for an indefinite period will have an infinite present value if it is not discounted. Thus, where no lump sum equivalent can be found to replace a cost that extends indefinitely, the evaluation horizon must be limited or discounting must be employed.

Flexibility of approach

An attractive feature of the methodology is that it provides a flexible framework for analysis that can readily accommodate inputs from a variety of sources. Waste management personnel, for example, may generate a number of threat scenarios that they consider to be the most relevant to a given situation. If, however, it becomes apparent that the public is largely concerned with some other threat, an appropriate scenario can be added without disrupting or contradicting the previous work.

DEMONSTRATION OF THE METHODOLOGY

This section provides a simple hypothetical example of the use of the methodology discussed above.

THE PROBLEM

You are the administrator of any agency responsible for hazardous waste in your area. A firm is installing a new process which will generate 250,000 cu.m. per year of an aqueous waste containing 50 parts per million of non-degradable toxic elements. The firm proposes to dispose of this waste by injecting it into a saline aquifer some 600 meters below their premises. They estimate that this will cost $50,000 per year (including capital charges) over a 20 year life span.

Your staff investigates other possibilities, and their findings are as follows:

(i) The waste stream can be reduced to 25,000 cu.m. per year with a corresponding increase in the concentration of toxic elements, at a cost of $20,000 per year to the firm.

(ii) The waste stream can be treated to provide an effluent that is acceptable to the municipal sewer. Treatment results in 250 cu.m. per year of a toxic sludge. The cost of treatment and effluent charges would be $115,000 per year.

(iii) There are two landfills that could accept either the liquid waste (from (i), above) or the sludge (from (ii)). The 'local landfill' is a publicly operated landfill located in a wet zone immediately adjacent to a river 50 km. from the generating firm. The 'secure landfill' is a privately operated chemical landfill located in a dry zone 360 km. from the firm. Transport to either landfill would be by truck.

(iv) Other possibilities for dealing with the waste (such as resource recovery or ocean dumping) are not available.

Hence, there are five technically feasible disposal plans, as follows:

(A) Deep well injection on the firm's premises.

(B) Sludge sent to the local landfill.

(C) Liquid waste sent to the local landfill.

(D) Sludge sent to the secure landfill.

(E) Liquid waste sent to the secure landfill.

THREAT SCENARIOS

The following scenarios represent the major threats. In-plant accidents under any plan are expected to have approximately similar impacts, and hence do not have to be evaluated.

Threat Scenario I: Water contamination from deep well injection

Drinking water is obtained from numerous wells that penetrate a shallow aquifer in the vicinity of the generating firm. This aquifer may become contaminated as a result of some unanticipated interconnection with the deep saline aquifer. The probability of this is unknown. If this happens, corrective action could be taken by providing temporary water supplies to the local residents, and by drilling several additional wells into the saline aquifer and counterpumping to reverse the migration of the waste. The total cost of this clean-up operation is estimated to be some $2,400,000; which would be considerably less costly than providing a permanent new water supply to the local residents.

Threat Scenario II: Leaching from the local landfill

If the liquid waste were discharged to the local landfill, it is assumed that the entire waste would quickly enter the river. If the sludge were deposited at this landfill an appreciable proportion of the toxic elements would probably be retained, but the above assumption could be used as the worst case. Either sludge or liquid waste contributes 12.5 tons of toxic elements per year. The river has a mean flow of 200 cu.m. per second implying a toxic element concentration of two parts per billion (ppb) if the waste was uniformly diluted. However, local concentrations are expected to be higher.

The river supports an important salmon fishery, and experts value a typical year's fishing at $800,000, excluding indirect effects such as tourist dollars brought into the region by the fishery. The experts expect the onset of high fish mortality to occur at toxic element concentrations somewhere between 20 and 100 ppb, but are reluctant to say what impact two ppb would have on the salmon due to effect variability with duration of exposure, alkalinity and the presence of other elements. They point out, however, that there is some evidence that fish avoid sub-lethal concentrations of toxic elements; hence the waste could conceivably decimate the fishery by discouraging the salmon from returning to spawn.

Threat Scenario III: Transport accidents

Statistics indicate that 50 accidents involving waste spills can be expected per billion kilometers traveled by truck in the region. The clean-up cost associated with a typical accident is estimated to be $10,000. Serious injuries and deaths directly attributable to the properties of the waste are expected to be negligible.

Threat Scenario IV: Flash flood at the secure landfill

The most likely threat from the secure landfill is contaminated run-off from a flash flood. Such a flood is expected to occur less than once per hundred years and damage along the flood path directly attributable to the toxic elements is expected to be minimal.

ANALYSIS OF THE ALTERNATIVES

Table 3 presents a comparison of the alternative plans. The gate fee for all wastes at the local landfill is $3.00 per cu.m. At the secure landfill it is $30.00 per cu.m. for the sludge and $20.00 per cu.m. for the liquid. Transport costs are $7.00 per cu.m. to the local landfill and $22.00 per cu.m. to the secure landfill.

As soon as the control costs are evaluated, it is possible to eliminate plans C and E because these plans are 'dominated' by B and D respectively. Dominance occurs when both the quantified costs and non-quantified costs are greater for one plan than another. Consider plan B versus plan C. The control costs for B are $117,500 per year versus $270,000 per year for C, and detailed evaluation is not necessary to show that the potential environmental damages from B are also less than from C. There is less possibility for release of toxic elements from the sludge (plan B) than from the liquid (plan C); while B requires less transportation than C, resulting in fewer accidents. Thus plan B is clearly preferable to plan C as both the quantified costs (the control costs) and the non-quantified costs (the environmental damage potential) are lower for B than C. Similar arguments apply to D versus E.

This reduces the number of plans to be evaluated to three (A, B and D). The next step is to examine the threats associated with each plan and to determine the nature of the effects of each plan on the parties-at-interest. These effects are summarized in Table 4.

The parties-at-interest most strongly affected in this example include the water supply authority, and to a lesser extent the water users near the plant, who would be concerned about the threat from deep well injection (Threat Scenario I). Fish experts would oppose plan B, although fishermen and related industry might perceive only a weak threat. Fishing interests might, however, have an unexpected ally. If plan A were prohibited, the generating firm itself could well prefer D over B. The annual cost of plan D is only $10,500 greater than plan B, while if the firm opted for B, it could receive adverse publicity if the fish threat (Scenario II) materialized. In contrast, the firm might enhance its reputation as a responsible environmental citizen if it sent its waste to the secure landfill under plan D. That the parties-at-interest analysis shows only negative impacts for plan B, confirms the unattractiveness of this plan in relation to A and D.

"IT'S YOUR DECISION"

The critical choice is between plans A and D, and involves reduced control costs and greater damage potential if A is preferred to D. If plan A is selected, the present value of the control costs discounted over the 20 year project is $664,000 less than for plan D. On the

TABLE 3. COMPARISON OF ALTERNATIVE PLANS

	PLAN				
	A	B	C	D	E
	Deep Well Injection	Local Landfill		Secure Landfill	
CONTROL COSTS (dollars)		Sludge	Liquid	Sludge	Liquid
Generator's annual costs					
-On-site operations	50,000	115,000	20,000	115,000	20,000
-Transport	-	1,750	175,000	5,500	550,000
-Gate fees	-	750	75,000	7,500	500,000
Total annual cost	50,000	117,500	270,000	128,000	1,070,000
Present value 20 years' costs discounted at 10% per year	426,000	1,000,300	2,298,000	1,089,700	9,109,500
Other control costs -Administration and monitoring	←	Not significantly different			→

	PLAN A	PLAN B	PLAN D
ENVIRONMENTAL IMPACTS			
In-plant accidents	←	Not significantly different	→
Major threat scenarios	I: Water supplies contaminated. Mitigation cost $2,400,000, plus cost of changing to another plan. Probability: not estimated.	II: Salmon fishery at risk. Direct value $800,000 per year. Indirect effects locally important. Probability: not estimated. III: Transport accident. Clean-up cost $10,000. Probability: $2x10^{-5}$/year	III: Transport accident. Clean-up cost $10,000. Probability: $1.4x10^{-4}$/year. IV: Contamination via flash flood. Damage potential slight. Probability: $< 10^{-2}$/year.
OTHER EFFECTS	Product prices would be slightly higher and/or generating firm's net income slightly lower with Plan B or D than with Plan A		

other hand, plan A poses the threat of water contamination (Scenario I) with its clean-up costs and the need to find an alternative disposal method if deep well injection does contaminate the water supply. The threats from transport accidents (Scenario III) and from flash floods at the secure landfill (Scenario IV) appear to be so minor that they can be neglected. Nevertheless it was important to

TABLE 4. PARTIES-AT-INTEREST ANALYSIS

The matrix characterizes the expected attitudes of the major parties-at-interest towards each plan.

Party-at-interest	**PLAN** **A**	**B**	**D**
Generating firm's management	++	--	-
Local water supply users	-		
Water supply authority	--	-	+
Fish experts	-	--	+
Fishermen, fish-related industry		-	
Environmentalists	--	-	+

Key: see Table 2

recognize them, and demonstrate (or obtain consensus judgment) that they could be disregarded.

If plan A was adopted, and problems with the deep well scheme developed after (say) five years, the additional costs of taking the correcting action described under Threat Scenario I and switching to plan D for the next 15 years would have a present value of $1,895,000. Is it worth risking $1,895,000 to save $664,000? If these data completely and accurately represented the choice, a decision-maker who was not risk adverse would support plan A if he believed that the probability that the threat would materialize was less than 35 percent. The probability that the threat will materialize is unknown. It may be one in two, 10%, 1%. . . . If, however, the threat materialized and correcting action as described in Scenario I failed, a completely new water supply might have to be brought in at a cost of tens of millions of dollars. Does society regard the risk as acceptable, or would it prefer to avoid risk and accept higher costs that would be passed on to consumers in the form of higher product prices or lower dividends? If the risk is to be taken, is the distribution of the risk and the benefits acceptable, or is there a way in which it can be made more equitable?

It's your decision!

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ECONOMICS OF DISPOSAL AND THE COMPILATION OF A DATA BASE FOR STANDARDS/REGULATIONS OF FGD SLUDGE

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ABSTRACT

Regulations regarding the control of sulfur dioxide emissions from power plants have suggested wet scrubbing of flue gas as the best means of meeting Best Available Control Technology emission levels, yet some disagreement exists as to how the resulting throwaway sludges can be disposed of in an environmentally acceptable fashion. Cognizant of this problem and its effect in deterring many plants from installing FGD systems, the EPA has sponsored a series of 19 studies aimed at evaluating the effectiveness of the various disposal methods. The purpose of this paper is to comment on the data base established thus far, and to project its potential impact on the promulgation of sludge disposal regulations.

The data base includes information in the following general areas:

- The technology of FGD sludge disposal;
- Environmental criteria by which to evaluate the various disposal options; and
- Existing or proposed regulations/standards which have been or could be applied to the disposal of FGD sludges.

The available methods of FGD sludge treatment and disposal are reviewed. Available cost information for these methods is summarized. The potential environmental impacts of FGD sludge disposal are enumerated, with supporting data from ongoing research efforts. The past and present federal and state regulatory approaches are reviewed as they relate to each of these impacts. Future regulatory approaches are discussed, with specific reference to SCS Engineers study findings and recommendations.

INTRODUCTION

The Clean Air Act and its amendments have established standards of performance for new fossil fuel-fired steam generators. Because of the lack of commercially available alternatives to conventional combustion technology, most utilities have chosen to use either low sulfur fuel or wet scrubbing flue gas desulfurization (FGD) systems to meet SO_2 emission limitations. A decline in low sulfur fuel use will result from the most recent Clean Air Act amendments.

The vast majority of planned and operational FGD systems employ lime or limestone as the sorbent. The by-product sludges from lime/limestone FGD are generated in large volumes and are typically disposed of in lagoons or landfills. The chemical and physical nature of these waste sludges has prompted EPA to investigate the environmental impact of FGD sludge disposal to land, and to demonstrate and develop treatment and disposal/utilization methods which are perhaps more environmentally acceptable.

SCS Engineers, Long Beach, California was contracted by EPA in 1975 to compile and analyze the findings of previous and ongoing FGD sludge disposal research.* It was recognized at that time that FGD sludge disposal would some day be regulated at the federal level. The study was therefore structured as a preliminary guideline development document using the data base established thus far as the basis for analysis. This paper summarizes the SCS findings.

INDUSTRY CATEGORIZATION

Description of Power Generating Facilities

In 1977, there were 1,040 fossil fuel-fired power plants operating in the United States, possessing a combined generating capacity of more than 320,000 megawatts. By 1994, 200 more plants with an additional 111,041 megawatts of generating capacity are projected to become operational. Of this 1994 capacity, 66 percent will fire coal exclusively. The remainder will use oil, natural gas, or a combination of oil and coal(1).

Under the federal Clean Air Act, power plants are responsible for emission control. For control of sulfur oxide emissions, the two most widely used methods are:

1. The use of a natural low sulfur fuel or partially desulfurized high sulfur fuel; and
2. Flue gas desulfurization (FGD).

The Clean Air Act Amendments of 1977 require the "best technological system of continuous emission reduction" and the "achievement of a percentage in..emissions.. from the use of fuels which are not subject to treatment prior to combustion."(2) In other words, low sulfur fuels and intermittent controls will not be acceptable as a means of compliance.

Non-regenerable processes account for approximately 90 percent of those FGD systems which are either operational or under construction. Lime and limestone systems are the most prevalent, with 75 percent of the scrubbers projected to be operational by 1980 utilizing these processes(3). The sodium-lime double-alkali systems thus far have been installed primarily on industrial fossil fuel-fired boilers. Scrubber systems regenerating sulfur or sulfuric acid have not yet gained very much acceptance in the United States. Only five full-scale projects are still in the active planning stages(4).

Table 1 lists the total committed FGD capacity through 1985 and the associated annual sludge generation.

Description of Industrial FGD Users

Many non-utility industrial scale fossil fuel-fired steam generators are also regulated by the new source standards. Most smaller boiler units are equipped for firing a variety of fuels and have achieved compliance by use of low sulfur fuels. A total of eight non-regenerable industrial scale FGD systems were on-line in June 1977 in the United States. Non-regenerable double-alkali FGD is the prevalent system for industrial steam generators.

Rationale for Subcategorization

The purpose of subcategorization within an industry category is to take into account basic differences in waste generation, treatment technology, and economics between plants for regulatory purposes. When discussing subcategorization for FGD sludge disposal regulation purposes, some of the same factors that entered into subcategorization during effluent guidelines development should be considered, but with several important differences: (1) FGD sludge is disposed to land, and (2) utility economics are regulated by the government. Economic subcategorization has been necessary in some other industries to prevent economic inequities and plant closures. Because costs for power generation are passed directly to the consumer, it would be a disservice to the power utility consumer to create an arbitrary subcategorization on the basis of "ability to pay."

The following variables were considered as rationale for subcategorization:

1. Size and age of plant;

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*"Compilation of Data Base for the Development of Standards/Regulations Relating to Land Disposal of Flue Gas Cleaning Sludges." EPA Contract No. 68-03-2352; July 1975.

TABLE 1. CUMULATIVE COMMITTED NON-REGENERABLE FGD CAPABILITY, 1975-1985 (MW)*++

	Lime Scrubbing	Limestone Scrubbing	Lime/ Limestone	Double Alkali	Total Capacity	Total Sludge Generation**
1975	475 (2)	1,954 (9)	20 (2)	32 (1)	2,481 (14)	1,225
1980	9,445 (23)	12,695 (35)	270 (3)	652 (3)	23,062 (64)	11,200
1985	11,515 (28)	13,445 (37)	797 (4)	+	26,409 (72)	13,300

*Numbers in parenthesis indicate number of scrubber units.

+None committed beyond 1980.

**Thousand metric tons of dry solids/year.

++Reference 5.

2. Type of plant or fuel;
3. Type of air pollution control and FGD equipment;
4. Untreated (raw) waste characteristics;
5. Disposal site characteristics.

The effects of plant operating variables upon the characteristics of FGD sludge are complex and difficult to predict. In addition, plants may often change fuel and/or operational procedures, thereby changing the FGD sludge characteristics. Therefore, it is deemed impractical to regulate FGD sludge disposal on the basis of type of plant or in-plant process. Sludge characteristics also vary substantially within the same plant and alone, do not provide a practical means of subcategorizing the industry.

Disposal site characteristics vary substantially between plants and result in associated differences in potential environmental impact. These characteristics set a need for differences in regulation between plants, and are therefore a logical means of subcategorization. Important site characteristics in this respect are:

- Present and future land values and possible uses;
- Groundwater resources (quantity and quality);
- Disposal site hydrology and mass transport potential (permeabilities, hydraulic gradients, impurity attenuation, flooding potential, etc.);
- Disposal site meteorology (evaporation and precipitation rates, etc.);
- Local ecology;
- Geographic location; and
- Acceptable land degradation.

SULFUR OXIDE CONTROL TECHNOLOGY

Utilities and other industries burning fossil fuels can select from three general categories of control systems to achieve compliance with standards:

- FGD systems with sludge generation
- FGD systems that produce a marketable product
- Control systems that do not generate a sludge

As of June 1977, 49 FGD systems were in commercial operation in the U.S. Of these, 41 were installed on utility plants and 8 on industrial fossil fuel-fired steam generators. Table 2 differentiates the number and capacity of these operational systems by FGD process. This table shows that the lime/limestone systems account for 34 utility scale systems and for more than 90 percent of the total scrubbing capacity. Double alkali systems currently dominate the industrial scale FGD market, although several of these smaller systems were conceived as pilot or demonstration facilities. Lime/limestone systems are expected to dominate the industry through 1985. An estimated 154 FGD systems are currently operational or at some phase of implementation or selection(5).

FGD Systems with Sludge Generation

Primarily nonregenerable FGD systems are employed by industries and utilities. Available options for nonregenerable FGD systems are:

- Lime scrubbing (tail end)
- Limestone scrubbing (tail end)
- Double alkali scrubbing (sodium, ammonia)
- Sodium carbonate scrubbing

These systems together comprise the de facto "Best Available Control Technology" under current New Source Performance Standards. The first two use lime and limestone, respectively as the scrubber sorbent, while the fourth uses sodium carbonate. In all three systems, the spent sorbent is not regenerated. In the double alkali system, sodium salts used as the sorbent are regenerated from the scrubber effluent through lime addition; the calcium-based precipitates are then disposed of. Sludge generation rates for lime, limestone, and double alkali systems are on the order of 0.06 to 0.12 tons of dry solids/MWh. The principal reasons for lime/limestone predominance is the low sorbent cost and greater availability.

FGD Systems Which Do Not Generate A Sludge

Regenerable FGD systems can have as their by-products gypsum, hydrogen sulfide,

TABLE 2. SUMMARY OF OPERATIONAL FLUE GAS DESULFURIZATION SYSTEMS +

FGD Process	Number in Operation*	Total MW Capacity *
Utility Scale		
Lime scrubbing		
Lime	12	3,897
Lime/alkaline ash	2	720
Limestone scrubbing		
Limestone	18	4,267
Limestone/alkaline ash	2	1,390
Wellman-Lord scrubbing	1	115
Dilute acid scrubbing	2	23
Sodium carbonate scrubbing	3	375
Magnesium oxide scrubbing	1	120
Industrial Scale		
Double alkali scrubbing	7	243
Sodium carbonate scrubbing	1	150

* For fossil fuel-fired steam generators as of June 1977.

+ Reference 4

sulfur dioxide, sulfur and sulfuric acid. Hydrogen sulfide and sulfur dioxide are gases with relatively little commercial value, while gypsum, elemental sulfur, and sulfuric acid are readily marketable. Certain FGD systems that remove and concentrate sulfur dioxide can either oxidize to sulfuric acid or reduce to elemental sulfur. Other systems directly produce sulfur or sulfuric acid. Currently, the most promising systems are:

- Dilute acid scrubbing
- Wellman-Lord scrubbing
- Magnesium oxide scrubbing
- Citrate scrubbing

Regenerable FGD technology producing elemental sulfur or sulfuric acid has a proven commercial market in certain areas. Marketing and utilization of FGD sludges or gypsum is currently under investigation by the EPA and other public and private organizations. Current market conditions, coupled with potentially higher FGD costs, have limited the commercial acceptance of these systems to date.

Lime/Limestone Sludge Utilization

In order to avoid the problems associated with FGD sludge disposal, research has been in progress in the area of nonregenerable sludge utilization. Technical developments for FGD sludge reuse have largely followed precedents established for the utilization of fly ash.

The current market for nonregenerable FGD sludge is very limited, and disposal is generally more cost-effective than recovery. Potential markets for FGD sludge include use as gypsum, structural landfill, synthetic aggregate, mine void backfill, soil amendment, and acid mine drainage control or treatment. Research has shown these alternatives to be technically feasible under proper conditions of treatment and control.

Other Non-Scrubbing Desulfurization Options

The high cost of wet scrubbing techniques has prompted many public and private institutions to seek alternate means for reducing SO_2 emissions. Some of these techniques are:

- Fuel switching from high sulfur coal to natural gas, oil, or low sulfur coal
- Coal cleaning
- Fluidized bed combustion
- Coal gasification

Many of the techniques are still in the developmental stages, but accelerated research may, in a few years, promote them to commercially available status.

Low sulfur fuel use, although the predominant means of compliance with SO_2 emission standards, will no longer be acceptable for this purpose in many instances. New Source Performance Standards prohibit the use of low sulfur coal for compliance. The Clean Air Act may also require some existing sources to use certain native coals which are higher in sulfur content than those obtainable elsewhere.

Coal cleaning has been practiced for many years and will be acceptable as a means of meeting Clean Air Act requirements. The predominant coal cleaning technologies remove pyritic (organic) sulfur by physical means, which can amount to a 30 to 70 percent reduction in coal sulfur content. Chemical means of organic sulfur removal have been developed and should see rapid commercial acceptance under the new law.

Fluidized bed combustion and coal gasification are both promising technologies, but should see limited full-scale application in the next decade.

CHEMICAL AND PHYSICAL PROPERTIES OF FGD SLUDGE

Many factors affect the chemical and physical characteristics of FGD sludge. These factors include:

- Characteristics of the fuel burned;
- Combustion equipment and operating parameters;
- Particulate collection mode;
- Scrubber operating parameters (liquid/gas ratio, slurry retention time, recirculation, etc.);
- FGD reagent and input water quality.

The impact of these factors could be controlled with modification in plant operation. This might be construed to mean that sludge characteristics can be modified to suit the disposal method and specific site characteristics. However, the power plant and associated gas cleaning equipment costs are generally much greater than sludge disposal costs. Overall system cost minimization will therefore generally require designs which minimize the FGD system cost, rather than optimize the sludge characteristics. Sludge characteristics can therefore be predicted, to some extent, using plant operating data. These chemical and physical characteristics are important to an effective disposal operation and have been the subject of most disposal-related research efforts to date. An extensive data base is becoming available.

Chemical Characteristics

The by-products of non-regenerable FGD systems are typically composed of four major constituents: calcium sulfate hemihydrate and/or dihydrate (due to mixed crystallization), calcium sulfite hemihydrate, unreacted sorbent, and fly ash. The relative amounts of these constituents are determined by the various scrubber and plant operating parameters discussed in the previous section. Table 3 shows the wide variation in sludge solid phase composition encountered in different FGD systems.

The solid phase of FGD sludge can also contain a variety of trace metals. These metals can come from several sources including fly ash, sorbent, makeup water or vapors in the flue gas itself. The metals which are contained in fly ash generally

TABLE 3. COMPOSITION OF SLUDGE FROM OPERATING SO_2 SCRUBBERS

Facility	Scrubber Sorbent	Sludge Composition (dry basis), wt percent $CaSO_3 \cdot \frac{1}{2}H_2O$	$CaSO_4 \cdot 2H_2O$	$CaCO_3$	Fly Ash	Comment
Lawrence	Limestone	10	40	5	45	
Hawthorn 3	Limestone	20	25	5	50	
Hawthorn 4	Limestone	17	23	15	45	
Will County 1	Limestone	50	15	20	15	
Stock Island	Limestone	20	5	74	1	Oil fired
La Cygne	Limestone	40	15	30	15	
Cholla	Limestone	15	20	0	65	14% $CaS_2O_3 \cdot 6H_2O$
Paddy's Run 6	Lime	94	2	0	4	
Mohave 2	Limestone	2	95	0	3	
Shawnee 1	Limestone	19-23	15-32	4-14	20-43	
Shawnee 2	Lime	50	6	3	41	
Phillips	Lime	13	19	0.2	60	9.8% CaS_3O_{10}
Parma	Dual Alkali	14	72	8	7	
Scholz 1A	Dual Alkali	65-90	5-25	2-10	0	
Utah	Dual Alkali	0.2	82	11	9	
Colstrip	Lime/Alkaline Ash	0-5	5-20	0	40-70	5-30% $MgSO_4$

*Reference 7.

are often dissolved in the waste slurry and enter the liquid phase; from there they may precipitate either as pure compounds or with the sulfate/sulfite crystals.

The liquid phase of FGD sludges is important due to its potential as leachate. The sludge liquors typically contain ions of sulfate, sulfite, chloride, calcium, magnesium, and various trace chemical species. The total dissolved solids (TDS) concentration in FGD sludges is a function of their equilibrium levels in the scrubber system, with TDS concentration in excess of 20,000 ppm being quite common in closed-loop operations. Table 4 lists the typical range of values for various species concentrations in the liquid phase.

TABLE 4.* CONCENTRATION OF CONSTITUENTS IN SCRUBBER LIQUORS

	Range of Constituent Concentrations at Potential Discharge Points	
Constituents	Mg/l (Except pH)	M
Aluminum	0.03 - 0.3	$10^{-5.95}-10^{-4.95}$
Antimony	0.09 - 2.3	$10^{-6.13}-10^{-4.72}$
Arsenic	<0.004 - 0.3	$<10^{-7.27}-10^{-5.40}$
Beryllium	<0.002 - 0.14	$<10^{-6.65}-10^{-4.81}$
Boron	8.0 - 46	$10^{-3.13}-10^{-2.37}$
Cadmium	0.004 - 0.11	$10^{-7.44}-10^{-6.01}$
Calcium	520 -3,000	$10^{-1.89}-10^{-1.12}$
Chromium (total)	0.01 - 0.5	$10^{-6.72}-10^{-5.02}$
Cobalt	0.10 - 0.7	$10^{-5.77}-10^{-4.92}$
Copper	< 0.002 - 0.2	$<10^{-7.50}-10^{-5.50}$
Iron	0.02 - 8.1	$10^{-6.45}-10^{-3.84}$
Lead	0.01 - 0.4	$10^{-7.32}-10^{-5.71}$
Magnesium	3.0 -2,750	$10^{-3.91}-10^{-0.95}$
Manganese	0.09 - 2.5	$10^{-5.79}-10^{-4.34}$
Mercury	0.0004- 0.07	$10^{-8.70}-10^{-6.46}$
Molybdenum	0.91 - 6.3	$10^{-4.71}-10^{-4.18}$
Nickel	0.05 - 1.5	$10^{-6.07}-10^{-4.59}$
Potassium	5.9 - 32	$10^{-3.82}-10^{-3.09}$
Selenium	< 0.001 - 2.2	$<10^{-7.90}-10^{-4.56}$
Silicon	0.2 - 3.3	$10^{-5.15}-10^{-3.93}$

TABLE 4* (Continued)

Constituents	Range of Constituent Concentrations at Potential Discharge Points: Mg/l (Except pH)	Range of Constituent Concentrations at Potential Discharge Points: M
Silver	0.005 - 0.6	$10^{-7.33}$-$10^{-5.25}$
Sodium	14 -2,400	$10^{-3.21}$-$10^{-0.98}$
Tin	3.1 - 3.5	$10^{-4.58}$-$10^{-4.53}$
Vanadium	<0.001 - 0.67	<$10^{-7.71}$-$10^{-4.88}$
Zinc	0.01 - 0.35	$10^{-6.82}$-$10^{-5.27}$
Carbonate	41 - 150 (as $CaCO_3$)	$10^{-3.39}$-$10^{-2.82}$
Chloride	420 -4,800	$10^{-1.93}$-$10^{-0.87}$
Fluoride	0.07 - 10	$10^{-5.43}$-$10^{-3.28}$
Sulfite	0.8 -3,500	$10^{-5.00}$-$10^{-1.36}$
Sulfate	720 -10,000	$10^{-2.12}$-$10^{-0.98}$
Phosphate	0.03 - 0.41	$10^{-6.50}$-$10^{-5.36}$
pH	3.04 - 10.7	$10^{-3.04}$-$10^{-10.7}$
Ionic strength		0.05 - 0.80

* Reference 8.

Physical Characteristics

The physical characteristics of FGD sludge solids are important to treatment process operations, disposal methods, and potential environmental effects. Of special interest are crystal morphology, bulk density, viscosity, and compressibility. Environmental considerations include permeability, settling characteristics, and load-bearing strength. Table summarizes the importance of various sludge properties to FGD sludge disposal operations.

Crystal Morphology--

Crystal morphology has perhaps the strongest influence on FGD sludge physical characteristics. Calcium sulfite hemihydrate is the predominant solid phase in most sludges. Sulfite crystals usually form in single flat plates, although spherical aggregated forms are also observed. In contrast, calcium sulfate dihydrate solidifies in blocky crystals. A limited amount of sulfate is soluble in the sulfite crystals, thereby making an unsaturated mode of operation possible. FGD sludge crystals are typically between 1 and 200 microns in diameter and classify as silt and silt loam under the U.S.D.A. system.

Bulk Density--

The bulk density of FGD sludges is another important physical characteristic. Bulk density determines such disposal-related parameters as compressibility, landfill volume requirements, permeability, and to some extent, compaction strength.

Bulk density of FGD sludge varies with sludge type (sulfate/sulfite), which in turn is related to the types of scrubber and coal. Mechanical dewatering of sludge does not substantially increase bulk density beyond that of settled sludge. Only high sulfate sludges with fly ash can exceed the optimal moisture content; this low dewatering effectiveness is typical of most FGD sludges.

Permeability--

Permeability, another important physical parameter, is related to the rate of flow of liquids through the material under a hydraulic driving force. This parameter enters into the calculation of the mass transport rate of contaminants from the disposal site to the groundwater.

FGD sludge permeability is dependent both upon size distribution and particle shape. Settled sulfite sludge is generally less permeable than sulfate sludge due to the irregular shape of the sulfite crystal aggregates. Settled and drained FGD sludges exhibit permeabilities of 10^{-3} to 10^{-4} cm/sec; light compaction will decrease this to 10^{-5} cm/sec, and even lower permeabilities have been attained on the laboratory scale using greater compaction and more extensive dewatering.

The presence of fly ash will decrease sludge permeability. The smaller fly ash particles fill in the sludge interstices, thereby blocking the movement of fluid through the media. Permeabilities of about 10^{-6} cm/sec have been achieved for a sulfate sludge mixed with fly ash; this is thought to be the minimum permeability achievable with untreated sludge.

Compressibility--

The compressibility, or compactibility, of FGD sludge is an important parameter when planning for disposal site operation and reclamation. The amount of compaction which can be achieved is dependent upon moisture content, crystal structure, and compaction force.

Studies of FGD sludge compressibility are documented in literature; one found that a sludge with equal quantities of sulfate and sulfite could be compacted to 1.3 g/cm^3 at 77 percent solids, but only 1.2 g/cm^3 at 72 percent solids. Similarly, a study of double alkali sludge achieved 1.15 g/cm^3 at 75 percent solids. Another study dealing with the effects of sulfate versus sulfite on compressibility found that higher sulfate concentrations in the solid phase reduced compressibility significantly(10). Laboratory experiments by the Aerospace Corporation have achieved bulk densities in excess of 1.44 g/cm^3; this represents a volume reduction of 25 percent for pure sulfite sludge, but only 7 percent for sulfate sludge(11).

Load-Bearing Strength--

Load-bearing strength is a partial function of compressibility, but also depends heavily upon the moisture content of the sludge. Sulfate sludge compaction strength has been shown to increase rapidly from 2.0 x 10^5 to 2.0 x 10^6 dynes/cm^2 below 35 percent moisture content. Since this moisture content can be achieved by mechanical dewatering, sulfate sludge can be made to support men and equipment if compacted. Japanese experience with high sulfate sludge (gypsum) production also indicates that this material will readily support grading equipment(12).

The load-bearing strength of sulfite sludge samples has been shown to increase gradually with decrease in moisture content. At 30 percent moisture content, the strength begins to increase markedly corresponding to the peak viscosity. The load-bearing capacity at this point was 2.1 to 2.4 x 10^6 dynes/cm^2. Even at low moisture content, however, the sludge may liquify if jarred or vibrated.

Despite the variation in load-bearing strength between sludges, certain generalities can be made. Light compaction will result in only a small improvement of strength. Settlement is unavoidable even after heavy compaction, although landfilled sludge settlement may be less than that of many common soils under these circumstances. Unconfined compressive strength is quite low, typically in the range of 7 to 14 x 10^5 dynes/cm^2.

Settling Characteristics--

The settling and dewatering characteristics of FGD sludge have been observed to be related to sulfite content. The flat plate structure of sulfite crystals results in water retention and a slower settling rate than the blocky sulfate crystals.

A study of sulfate/sulfite settling and the associated design considerations has concluded that the percent sulfite oxidation to sulfate has little effect on the required thickener diameters, provided the higher final moisture content can be tolerated when preparing for vacuum filtration(13). The primary difference in sulfite sludge settling rates is in the crystal plate size. Smaller plates entrap more liquor during the compression stage due to a higher incidence of inner-particle touching; thicker sulfite slurries take longer to reach the compression stage.

TREATMENT AND DISPOSAL TECHNOLOGY

Treatment of FGD Sludges

Three forms of FGD sludge treatment are considered state-of-the-art technology:

- Dewatering;
- Stabilization (fixation); and
- Forced oxidation.

Each process is designed to reduce disposal costs and/or reduce the potential environmental impact of disposal to land.

Dewatering--

Dewatering reduces the volume of sludge, removes and recirculates water, and improves sludge handling characteristics. Dewatering processes with demonstrated or potential applicability to scrubber sludges are:

- Clarifiers
- Centrifuges
- Vacuum filters
- Solar evaporation ponds
- Bed dryers
- Thermal dryers

The first four processes listed above have been applied to scrubber sludges, and operating experience is documented. The other processes listed have not been applied to scrubber sludges, but have been used successfully for other types of industrial and municipal sewage sludges.

Clarifiers are standard equipment on most FGD systems. The underflow from these units can contain 15 to 35 percent solids. Centrifuges and vacuum filters are gaining popularity for FGD sludge dewatering. Dewatering of 50 to 80 percent solids has been documented using these devices; actual dewatering efficiency depends upon the chemical characteristics of the sludge and the presence of fly ash. Solar evaporation ponds serve both disposal and treatment functions. Disposal pond supernatant is often recirculated, and the settled sludge ranges from 40 to 65 percent solids in most applications.

Stabilization--

Stabilization techniques employed thus far have incorporated such power plant wastes as fly ash and bottom ash, thereby consolidating several waste disposal activities into one activity. Stabilization can reduce the volume required for disposal through the mechanical dewatering operations included in some systems. Since pozzolantic stabilization improves the load-bearing and handling characteristics of sludge, such materials can be used as a fill material for road base, berms, embankments, and dams(14). In addition, stabilized sludge often has less pollution potential than raw sludge. This is because the stabilization process normally restricts the movement of water through the sludge and/or chemically binds the contaminants so they are less readily dissolved by permeating water.

As of December 1977, at least 15 power plants employed some form of sludge stabilization. Of these, 7 employ commercial stabilization processes and/or services. The remainder typically use fly ash, bottom ash, and/or lime as additives. The product, in these cases, is a physically stable material which can be transported like soil and disposed of as landfill material.

A variety of commercial stabilization processes and services are available for FGD sludge treatment. Several of these services use a proprietary additive or process. IU Conversion Systems (IUCS) offers a patented treatment procedure using the lime-fly ash reaction to produce a structurally stable and low-permeability material. Dravo Lime Company offers a stabilization service utilizing a proprietary additive, Calcilox^R, which after a curing of 2 to 4 weeks, will solidify either in a landfill or under water. Other proven stabilization processes are available commercially for hazardous waste treatment, but high processing and additive costs have precluded their use for FGD sludge treatment.

Each type of stabilization process results in a material with a different set of physical and chemical properties. Research has been under way for several years to evaluate existing stabilization processes and to develop new processes. Thus far, the most extensive studies of stabilized sludge and its properties have been completed by the Aerospace Corporation for EPA(15), the Army Corps of Engineers Waterways Experiment Station for EPA(16), and IU Conversion Systems(17,18).

All of the above research efforts have concluded that commercial stabilization improves the physical properties of FGD sludge. Sludge permeability is typically reduced by 1 to 2 orders of magnitude, depending on the physical nature of the treated sludge. Load-bearing strength is also improved substantially, particularly when treating sulfite sludges. Sulfate sludges (70 to 80 percent solids) have been shown, in some instances, to possess similar handling and load-bearing properties to stabilized sludge, but this is more the exception than the rule for sludge, as generated by FGD systems.

Stabilization, as well as providing a structurally improved product, may also reduce the rate of mass transport of soluble contaminants from the FGD sludge. This can be accomplished through a reduction in permeability/porosity and through chemical bonding of contaminants within the stabilized matrix.

The above-mentioned studies have shown that stabilization will result in a significant reduction in pollutant mobility. Aerospace(19) reported a 50 percent reduction in TDS loading between the first pore volume displacements in stabilized FGD sludge over that encountered for unstabilized sludge; more substantial reductions were experienced in subsequent pore volume displacements. While each study has used a different leaching test, the combined results seem to indicate that the principal means of pollutant mobilization from stabilized sludge is through the initial surface washing. Further leaching of contaminants from the sludge mass is limited by: (1) the low permeability and low hydraulic driving force (unsaturated) and (2) some apparent level of complexation or chemical binding within the sludge matrix due to stabilization.

Disposal of FGD Sludges--

The general categories of available disposal options include:

- Ponding (lined or unlined)
- Landfill
- Disposal to oceans
- Disposal to mines (backfill)

The use of unlined disposal ponds is typically the least expensive method of sludge disposal. This technique, however, has been subject to criticism, primarily due to the potential for sludge contaminants to enter the groundwater. Nonetheless, a majority of the FGD sludge disposal systems in operation use unlined ponding for either intermediate clarifying or ultimate disposal. The use of unlined ponds for sludge disposal is expected to continue pending regulation of the practice. "Unlined" refers to the use of compacted indigenous soils as the liner material in situations where such soils are deemed adequate by local regulatory agencies.

Pond liners have been required in several instances. Typical liners are composed of imported natural clay. Artificial or synthetic liner materials have not been used for full-scale FGD sludge disposal ponds, but considerable research and cost analysis have been performed for this alternative.

The use of landfills for FGD sludge disposal is also prevalent. Backfilling of impoundments is the predominant mode. Landfilling requires that the sludge be either physically stabilized or thoroughly dewatered. The principal operational difference between sludge landfills and ponds is that sludge liquors are recycled at the plant instead of from the pond; this results in a significant land saving and allows for access to remote disposal sites by truck.

Ocean disposal of FGD sludges is an option that is perhaps available to non-regenerable FGD system users with economic access to the ocean. New ocean disposal initiatives are discouraged by regulatory agencies.

The feasibility of FGD sludge disposal to mines is of particular interest to the many mine-mouth, coal-fired power plants. Sludge disposal to mines has the advantages of: (1) minimal transportation requirements, when a mine is nearby; (2) minimal incremental land use; (3) possible mine reclamation; and (4) serving as a pH amendment for mine tailings. The principal concerns are possible interruption of mining operations, contamination of ground and surface waters, and fugitive emissions and runoff. The use of FGD sludge as mine backfill is currently being studied by several state and federal agencies(20).

ENVIRONMENTAL IMPACT OF FGD SLUDGE DISPOSAL

Those aspects of FGD sludge disposal which contribute to potential environmental impacts include:

- Disposal site characteristics
- Health effects of sludge components
- Safety
- Other ecological considerations

The specific impacts relating to each aspect are discussed below.

Disposal Site Characteristics

The disposal site characteristics which influence the environmental impacts of FGD waste disposal include:

- Present and projected land use
- Topography
- Hydrology and geology
- Meterology

These site characteristics, when combined with the sludge characteristics, economics, and other disposal variables, will determine the optimal solution to the disposal problem. The variety of these relationships indicates that no general solution is appropriate to all areas.

Present and Projected Land Use--

The present and potential future land use of a proposed disposal site will influence the disposal technique to be utilized. A primary distinction can be made between urban and rural land uses. Property values are typically higher in urban locations than in rural areas. Therefore, techniques which utilize less land and/or generate a fill material of adequate bearing strength would be more desirable in urban areas.

Potential land use will be at least partially determined by present methods of FGD sludge disposal. For example, depending upon sludge characteristics, pond disposal of untreated sludge may result in a site with virtually no bearing strength. In urban locations, this lack of mechanical stability would prevent future use of the site for anything more than the lightest duty applications.

Topography--

Topography of the disposal site and adjacent areas influences the potential environmental impact of the disposal operations in four ways:

- o Rainwater runoff may flow naturally into the disposal area, increasing the hydraulic head;
- o Topography may allow sludge released by retention structure failure flow to nearby surface waters;
- o The relative elevations of the disposal pond surface, pond bottom, and groundwater have a strong influence upon the mass transport of FGD contaminants to the groundwater; and
- o Topography can control the visibility of the disposal site operation.

Hydrology and Geology--

The impact of the FGD disposal site upon the groundwater resources below the site is of major concern. Of particular interest is the mass transport of contaminants from the FGD sludge to the groundwater. This process is a function of:

1. Quality and quantity of leachate generated by the in-place sludge;
2. The rate at which leachate permeates through the retention structure or a pond liner;
3. The rate at which individual contaminants in the leachate which escapes the retention structure travel through the underlying soil; and
4. The effect of the contaminants which reach the groundwater aquifer upon the quality of the groundwater.

Groundwater quality can range from highly desirable drinking water to water that is nonpotable. These variations in existing groundwater quality can be of natural or artificial origin. In many areas of the southwest, it is common to find shallow, highly saline water due to concentration by evaporation or a preponderance of exchangeable cations. The water quality in many of these areas may be worse than the quality of the leachate generated in a disposal site.

Where potentially useful water underlies a disposal area, it is necessary to consider the mass transport of contaminants from the site to the water table, in order to evaluate the potential environmental significance of any given disposal practice. The term "mass transport" as it is used here, refers to the movement of contaminants from a disposal site to the surrounding environment. The rate of mass transport is perhaps the most important factor in estimating groundwater pollution potential.

Different disposal techniques or site variables affect the mass transport by changing the controlling parameters. For example, clay liners in the bottom of ponds will reduce the flow rate through the bottom of the pond by decreasing the permeability; while locating a pond in a high water table, low horizontal hydraulic gradient area will decrease the mass transport by decreasing the hydraulic gradient. This will also decrease the flow rate. Locating the disposal site above clay and/or organic soils which have high cation exchange capacity will increase the retention factor. This will decrease the mass transport of some contaminants by slowing cation movement.

Meteorology--

Local meteorology can interact with the disposal technique being employed through two primary mechanisms. The first of these relates to the characteristic evaporation/precipitation ratio at the site, and the second to the effects of wind erosion on the surface of the site if the site is dried.

Evaporation/Precipitation--In areas with high evaporation rates relative to precipitation rates, significant amounts of water can be evaporated from a pond. The net evaporation rate can vary from a fraction of a meter per year to up to 2.5 meters annually. A high evaporation rate allows certain types of solutions to disposal problems that are not feasible in low evaporation rate areas. Under such climatic conditions, contaminated leachate can be disposed of through evaporation.

Wind Erosion--The second possible effect of local meteorological conditions is surface wind erosion. If the disposal site dries out and is not supporting vegetative cover, wind can erode the surface material and remove it from the site. The importance of this phenomenon will vary from area to area.

Covering a site with soil to establish a vegetative cover will help stabilize the site, as is done with dry ash disposal. Observations of FGD sludge disposal sites in the southwestern United States indicate that the surface can also be stabilized by bottom ash. When both fly ash and bottom ash are disposed of at the same site, the wind erodes the loose fly ash from between the mixture of fly and bottom ash, leaving a surface covered only by bottom ash. Bottom ash particles tend to be too large for wind erosion. Once this bottom ash surface is formed, the site is stabilized against further wind erosion. The proper selection of cover materials is certainly preferable to sprinklers and other dust control methods due to limited maintenance.

Health Effects

The dissolved salts, trace metals, and other contaminants contained in FGD sludges are all found in man's natural environment. Through evolution man has acquired a tolerance for these contaminants and requires many of them in his diet for good health. A typical biological response curve would show an increasingly beneficial effect with increasing contaminant concentrations to a certain level. Beyond this level there is a tolerance region beyond which benefits decrease, injurious effects begin, and finally, a lethal concentration is reached The goal of FGD sludge management is not to reduce contaminant levels to zero, but rather to ensure that the concentrations of the contaminants which could eventually return to man and other biota are not at harmful levels.

Contaminant Pathways--

The potential health problems posed by sludge disposal can be approached by examining contaminant pathways to man. Adding an FGD system to a power plant effectively removes trace contaminants from the atmospheric pathway to man and places the contaminants instead into useful water. This converts a regional atmospheric pollution problem into a potential local water pollution problem.

Groundwater--The major potential pollution problem in FGD sludge disposal is the transport of leachate contaminants from the disposal site into local potable groundwater supplies. Predicting the potential mass transport of specific contaminants to man via this pathway is complex and involves the following major variables:

- The flow rate of the leachate from the disposal site into the aquifer, which is dependent upon such factors as permeability of the soils and liner (if any) underlying the disposal site, and the hydrostatic head force upon the leachate;
- The concentration of the specific contaminants contained in the leachate generated by the disposal site, and the changes occurring in these concentrations due to attenuation effects by the soil during passage of the leachate to the aquifer;
- The capability of the aquifer through actual replenishment to dilute the leachate reaching it, i.e., the relative volumetric rate of: (1) the leachate reaching the aquifer, (2) the replenishment by natural sources such as horizontal groundwater migration, (3) the rate of water supply withdrawal, and finally (4) the extent of the mixing which occurs in the aquifer between leachate and natural source water; and
- The contaminant concentrations of the natural source water in the aquifer and their relation to concentrations of similar contaminants in the leachate reaching the aquifer.

The above-listed variables are often interrelated, complex, and difficult to measure accurately. Considering, however, the large size and costs involved in FGD sludge treatment and disposal, the effort to evaluate these factors should be cost-effective in designing the best sludge management system for a particular site.

Surface Waters--A second pathway by which contaminants contained in FGD sludge may reach man is by way of surface waters. Considering the initial concentrations of the contaminants in question and the dilution capabilities of the surface waters adjacent to many power plants, the levels of contaminants reaching man from sludge supernatant discharge will be site-specific.

Health Significance of Sludge Contaminants--

The health effects of metals and their compounds are often difficult to quantify. Of the heavy metals found in FGD sludge, five elements (arsenic, lead, mercury, fluoride, and selenium) represent known hazards to human health based on existing evidence. Lead, mercury, and cadmium are particularly insidious because they can be retained in the body for relatively long periods of time, thus functions as cumulative poisons(21). Table 5 provides a comprehensive summary of the presence of metals in the environment, their toxicity to humans, and their half life in the body.

In the liquid phase, trace element concentrations are important in determining the potential heal hazards of leaching or surface water discharge of FGD sludges.

A summary of concentration ranges common to various sludges and effluents was given in Table 4. The range of data shown in the table for sludge leachates/elutriates represents a wide variety of power plants and scrubber systems.

The following conclusions can be drawn regarding the health significance of leachate and surface water discharges from disposal systems:

- All studies agree that the total dissolved solids in the sludge liquors exceed drinking water standards;
- All studies indicate that the selenium concentration commonly exceeds drinking water standards;
- Selected data indicate that, in some instances, fluoride concentrations may be high;
- All studies indicate that arsenic, lead, and mercury (among others) can exceed drinking water standards in some instances, although typically below standards and readily attenuated by most soils.

Safety

Safety considerations associated with the disposal of FGD sludges can be directed toward three groups: (a) workers employed at the site; (b) the general public; and

TABLE 5. METALS IN THE ENVIRONMENT AND THEIR TOXICITY*

Metal	Average daily intake (μg/d)		Oral dose producing toxicity (mg)	Fatal dose (ingestion)	Total body content (mg)	Whole body half-life (days)
	Food and Water	Air				
Antimony	100	1.7	100	100-200 mg	7.9	38
Arsenic	400-900	--	5-50	120 mg	15-20	280
Barium	735	30	200	1 g	22	65
Beryllium	12	0.04	--	not known	0.3	180
Cadmium	160	7.4	3	not known	50	200
Chromium	245	1.1	200	5 g	1.8	616
Copper	1,325	11.4	50-250	10 g^{b}	72	80
Iron	15,000	84	--	5-10 g^{c}	4,200	800
Lead	300	46	--	0.5 g	120	1,460
Manganese	4,400	28.8	not known	--	12	17
Mercury	25	--	--	20 mg - 1 g^{d}	--	70^{e}
Nickel	600	2.36	--	--	10	667
Selenium	62	--	5	--	14.6	11
Silver	60-80	--	60	2 g^{f}	1	5
Tin	7,300	0.6	2,000	--	17	35
Zinc	14,500	16.8	--	10 g^{g}	2,300	933

* Ref. 21.

b. Copper sulfate
c. A two-yr old child
d. Mercuric salts
e. Methyl mercury
f. Silver nitrate
g. Zinc/sulfate

(c) livestock and wild animals. These safety considerations relate to the physical rather than the chemical properties of the sludge.

The thixotropic nature of certain untreated (typically "sulfite") FGD sludges poses an unusual safety hazard. A pond filled with such material may develop an apparently solid surface crust which may liquify on impact (such as a person jumping or a vehicle braking on the surface).

Ecological Considerations

FGD sludge disposal operations have potential for adverse impact on the surrounding ecosystem. Of primary concern are:

- The aquatic environment;
- The terrestrial environment;
- Irrigated agriculture and livestock.

Aquatic Environment--

Sludge disposal may affect the aquatic environment through either accidental release to a waterway or through intentional discharge to surface or groundwater. Surface and groundwater discharge is generally continuous; accidentla discharge is a random, possibly catastrophic event.

Since large volumes of cooling water are required to operate a fossil fuel-fired power plant, most plants are located near a large body of water. Installation of FGD units on these power plants entails a large number of pipes to carry the slurries around the scrubber and associated materials handling systems. Pipelines may also carry the sludge to disposal areas. Depending upon system design, a pipeline break could result in the accidental discharge of the slurry into a watercourse. Dike failure at the disposal pond may release several years' supply of sludge into a waterway in only a few hours.

It is estimated that the COD in one 300 hectare-meter sulfite sludge pond would be sufficient to remove all the dissolved oxygen from virtually any lake or several hundred miles of a large river. However, in a lake-type environment, rapid settling of the sludge would limit the impact to that of the immediate area of discharge(22).

In addition to accidental discharges to surface waters, water from an FGD sludge pond can enter the aquatic environment through: (1) an intentional direct discharge to surface waters or (2) percolation of pond water through underlying soils to groundwater supplies. The possibility of a direct surface discharge depends upon details of disposal site design, Percolation rates will again depend upon local site characteristics and disposal techniques.

Irrigated Agricultural Considerations--

When estimating the potential impact of FGD sludge leachate or liquor on irrigated agriculture, the most important contaminants are TDS, selenium, and boron. None of these is readily absorbed by soils. These contaminants can therefore enter the ground or surface waters. After leaving the site, these impurities may enter an irrigation system. The adverse impact of these components on agricultural lands is documented. A high TDS concentration in irrigation water requires modification of irrigation practices in order to prevent high salinity in the root zone of the plants.

Livestock--

The effects of FGD sludge liquor consumption on livestock could conveivably be a local problem under unusual circumstances. The salt tolerance limits of domestic livestock are specific to each animal, although generally between 3,000 to 12,000 ppm. As FGD sludge pond supernatant is ordinarily at the low end of this range, minimal dilution would render the leachate or supernatant harmless in terms of TDS.

The metals and toxic anions noted previously under Health Effects are equally important here. Metals such as lead and mercury are accumulated in animals and man alike, and could present a problem with livestock. The available chemical form of each element is important, but further investigation of speciation is necessary.

Aesthetics and Land Use

The aesthetic impact of an FGD sludge disposal operation is strongly site-specific. Local variables include public proximity, appearance of the operation, and site reclamation potential. Untreated sludge ponds resemble other common ponding operations, e.g., ash ponds, sewage lagoons, raw water supplies, storage reservoirs, etc. Obviously, disposal site location, grading, landscaping, and access roads should be selected to minimize public view and proximity to the site.

SELECTION OF CHEMICAL AND PHYSICAL REGULATING PARAMETERS

Rationale for Chemical Regulating Parameters

Various rationale are available for establishing chemical regulating parameters. Because groundwater and surface water protection are of primary concern, the regulating parameters for FGD sludge disposal should be associated with the liquid phase.

The significant chemical characteristics are the liquid phase concentrations of TDS, boron, fluoride, mercury, lead, and selenium. The selection of a regulating parameter from among these components should satisfy the following criteria:

- Accurate correlation with environmental impacts;
- Usefulness as an indicator of the migration of many contaminants, aside from itself;
- Simplicity of measurement;
- High measurement accuracy and reproducibility; and
- Low analytical cost.

Of the contaminants listed, TDS provides the best indication of overall contaminant migration, due to limited attenuation and ion exchange. TDS is also the simplest and least expensive contaminant to measure. In view of these considerations, it appears that TDS is the best chemical regulating parameter for FGD sludge disposal. While TDS should be used to monitor contaminant migration, concentrations of other contaminants should also be measured in the leachate to confirm the mass transport calculations.

Rationale for Physical Regulating Parameters

The physical properties of FGD sludges are important to the following disposal site considerations:

- Future land use;
- Rate of mass transport of contaminants from the site, as a factor of in-place sludge permeability; and
- Sludge flow during accidental release (particularly to a flowing stream).

Physical characteristics relating to these considerations include load-bearing strength, viscosity, and permeability. How many, if any, of these characteristics are important to a particular site are site-dependent.

The use of physical "stability" as a regulating parameter is subjective. While stabilization may be desirable for site reclamation in urban areas, the disposal of an unstable material (slurry or thixotropic solid) may be acceptable in areas of limited land use or value. The use of an absolute measure of stability for regulating all disposal operations is therefore not recommended.

The chemical and physical characteristics of FGD sludge set needs for regulation. Such regulations should emphasize the site and sludge characteristics.

ECONOMICS OF FGD SLUDGE DISPOSAL

The FGD sludge disposal cost data base has expanded rapidly since 1976. This expansion has been due to both the completion of several important economic studies (conceptual) and the publication of sludge disposal costs for several operating systems. The principal cost studies have been performed by the Aerospace Corporation (1976)(23), TVA (1977)(24), and Michael Baker, Jr., Inc. (1977)(25).

The principal factors affecting FGD sludge disposal economics include:

1. Type of coal;
2. Characteristics of the air pollution control system (wet and/or dry collection, type of sorbent, etc.);
3. Plant size, sludge generation rate;
4. Distance from plant to disposal site;
5. Geographic location (land cost/availability); and
6. Site characteristics.

The following cost estimates are in all cases based on one or more model power plants, each of which has subtle but important differences in the model plant definition.

Aerospace Corporation (1976)

The Aerospace studies have developed and updated detailed cost estimates for a variety of disposal alternatives, including lined ponding (natural or synthetic liner) and chemical fixation. Their most recent findings, presented in Table 6, show chemical fixation to be 2 to 3 times as expensive as ponding with a natural clay liner. Costs are based on conditions at a model midwestern power plant.

Tennessee Valley Authority (1977)

The TVA study of FGD sludge disposal economics developed comparative cost estimates for four disposal alternatives at each of 27 model plants (base case plus variations). Table 7 shows the relative ranking of the four alternatives for each model plant, based on annual revenue requirements. In general, the study found fixation costs to be competitive with those of untreated sludge disposal in many cases. The base case analysis, for example, showed IUCS fixation to be only 50 percent more expensive than untreated sludge disposal (compared to the Aerospace difference of 100 to 200 percent).

The extensive data base developed by TVA also permitted a detailed sensitivity analysis to be performed. The relative effect of 17 case variations on disposal costs for the 4 alternatives is presented in Table 8. The most important variables were shown to be distance to the disposal site and plant size. Other variables had a substantial effect on individual processes, which manifested itself in the broad range of costs between case variations. For example, the IUCS and untreated disposal alternatives were shown to have equal annual revenue requirements for one case variation (10 mi to disposal site), and yet another

TABLE 6. SLUDGE DISPOSAL COST RANGES (UNTREATED AND CHEMICALLY TREATED LANDFILLS, 1000-MW STATION, 50 PERCENT LOAD FACTOR, 30-YEAR AVERAGE, JANUARY 1976 DOLLARS)

Disposal Method	Base Material	\$/Ton Sludge[a, b] (Dry)	\$/Ton Coal[b]	Mills/kWh[b, c, d]
Untreated				
Pond	Natural Clay[e]	3.50	1.00	0.4
Pond	Liner[f]	5.70-7.80	1.60-2.20	0.7-1.0
Chemically Treated[g]	Indigenous Soil	7.30-11.40	2.10-3.20	0.9-1.4

[a] 510,000 short tons/year average (dry basis) including fly ash.

[b] Coal burned at rate of 0.88 lb/kWh, 3% sulfur, 12% ash, 85% SO_2 removal, 1.2 $CaCO_3/SO_2$ mole ratio.

[c] Land costs at \$1000/acre are included (equivalent to \$0.25/ton sludge, dry).

[d] Disposal within 5 miles of power plant.

[e] Assumes coefficient of permeability of clay is 1×10^{-6} cm/sec or better.

[f] Ponding costs cover range based on low-to-high material costs, i.e., PVC-20 (low) to Hypalon-30 (high).

[g] Chemical fixation costs vary, depending on characteristics of the waste and the disposal process chosen.

*Reference 26.

TABLE 7.* SUMMARY OF TOTAL ANNUAL REVENUE REQUIREMENTS[a]

ALL PROCESSES

Case	Untreated		Dravo		IUCS		Chemfix	
	Annual amount, k$	Mills/kWh	Annual amount, k$	Mills/kWh	Annual amount, k$	Mills/kWh	Annual amount, k$	Mills/kWh
Base case[b]	3,280[c]	0.94[c]	6,701[d]	1.91[d]	5,291[e]	1.51[e]	6,988[f]	2.00[f]
Variation from base case								
200 MW new	2,014	1.44	3,643	2.60	3,567	2.55	4,529	3.24
200 MW existing, 25 yr remaining life	1,841	1.32	3,672	2.62	3,699	2.64	4,695	3.35
200 MW existing, 20 yr remaining life	1,605	1.15	3,461	2.47	3,725	2.66	4,730	3.38
200 MW existing, 15 yr remaining life	1,433	1.02	3,390	2.42	3,822	2.73	4,856	3.47
Existing 25 yr remaining life	2,906	0.83	6,377	1.82	5,402	1.54	7,152	2.04
Existing 20 yr remaining life	2,135	0.70	5,961	1.70	5,430	1.55	7,191	2.05
Existing 15 yr remaining life	2,130	0.61	5,728	1.64	5,559	1.59	7,359	2.10
1500 MW new	6,746	0.64	14,264	1.36	10,411	0.99	14,362	1.37
1500 MW existing, 25 yr remaining life	5,827	0.55	13,821	1.32	10,656	1.01	14,769	1.40
1500 MW existing, 20 yr remaining life	4,726	0.45	12,749	1.21	10,684	1.02	14,791	1.41
1500 MW existing, 15 yr remaining life	3,969	0.38	12,138	1.16	10,900	1.04	15,053	1.43
12% ash in coal	2,902	0.83	5,924	1.69	4,533	1.30	6,229	1.78
20% ash in coal	3,609	1.03	7,406	2.12	5,971	1.71	7,600	2.17
2% sulfur in coal	2,639	0.75	5,316	1.52	4,654	1.33	5,935	1.70
5% sulfur in coal	3,869	1.10	8,007	2.29	6,188	1.77	8,263	2.36
200 MW, no flyash	1,495	1.07	3,063	2.19	3,396	2.43	3,766	2.69
No flyash	2,289	0.65	5,073	1.45	4,650	1.33	5,184	1.48
1500 MW, no flyash	4,546	0.43	10,448	1.00	8,162	0.78	9,771	0.93
5 mi to disposal	5,527	1.58	8,124	2.32	6,490	1.85	8,675	2.48
10 mi to disposal	7,504	2.14	9,360	2.67	7,475	2.14	10,003	2.86
Fixation additive rate - variation 1	-	-	6,052	1.73	4,994	1.43	13,651	3.90
Fixation additive rate - variation 2	-	-	7,577	2.16	5,511	1.57	10,099	2.89
Lime scrubbing process	3,136	0.90	6,168	1.76	5,093	1.46	6,200	1.77
Intermediate ponding and truck to landfill	-	-	6,620	1.89	-	-	-	-
Transport by truck to disposal area	-	-	-	-	-	-	6,698	1.91
Clarify (35% solids) and pump 1 mi	3,694	1.06	-	-	-	-	-	-
Clarify (35% solids) and pump 5 mi	5,195	1.48	-	-	-	-	-	-
Clarify (35% solids) and pump 10 mi	6,450	1.84	-	-	-	-	-	-
Clarify, filter (60% solids) and truck 1 mi	3,809	1.09	-	-	-	-	-	-
Clarify, filter (60% solids) and truck 5 mi	4,925	1.41	-	-	-	-	-	-
Clarify, filter (60% solids) and truck 10 mi	5,818	1.66	-	-	-	-	-	-
200 MW, constrained pond acreage (50% of optimum)	2,462	1.76	4,423	3.16	-	-	-	-
200 MW, constrained pond acreage (75% of optimum)	2,033	1.45	4,136	2.95	-	-	-	-
Constrained pond acreage (50% of optimum)	4,119	1.18	9,109	2.60	-	-	-	-
Constrained pond acreage (75% of optimum)	3,365	0.96	7,901	2.25	-	-	-	-
1500 MW, constrained pond acreage (50% of optimum)	8,985	0.86	20,366	1.94	-	-	-	-
1500 MW, constrained pond acreage (75% of optimum)	7,037	0.67	17,290	1.65	-	-	-	-
Pond settled density(40% solids)	3,747	1.07	-	-	-	-	-	-
Pond settled density(60% solids)	2,949	0.84	-	-	-	-	-	-
Unlined pond	2,765	0.79	-	-	-	-	-	-
Synthetic pond lining ($1.50/yd²)	3,882	1.11	-	-	-	-	-	-
Synthetic pond lining ($2.50/yd²)	4,253	1.21	-	-	-	-	-	-
Synthetic pond lining ($3.50/yd²)	4,590	1.31	-	-	-	-	-	-
Synthetic pond lining ($4.50/yd²)	4,900	1.40	-	-	-	-	-	-

a. Basis: Midwest plant location; mid-1980 operating costs; 7,000 hr/yr on-stream time.

b. New 500-MW plant; 30-yr life; coal analysis (by wt): 3.5% S (dry basis), 16% ash; flyash and SO_2 removed together to meet NSPS, limestone process with 1.5 stoichiometry based on SO_2 removed.

c. Direct ponding of 15% slurry; clay-lined pond; 1 mi from scrubber facilities; 50% solids settled density.

d. Ponding of 35% solids slurry; clay-lined pond; pump 1 mi to pond from scrubber facilities; 50% solids settled density in pond; treated with Calcilox (7% of dry sludge) and Thiosorbic lime (1% of dry sludge).

e. Landfill disposal of 60% solids material; 1 mi to landfill from scrubber facilities, trucks used for transport of treated sludge; treated with lime (4% of dry sludge).

f. Landfill disposal of 60% solids material; 1 mi to landfill from scrubber facilities; pipeline used for transport of thickener underflow to disposal and treatment area, treated with Portlant cement (7% of dry sludge) and sodium silicate (2% of dry sludge).

*Reference 27.

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TABLE 8*. EFFECTS ON TOTAL CAPITAL INVESTMENT AND ANNUAL REVENUE REQUIREMENT BY CASE VARIATIONS FOR ALL PROCESSES

	Degree of change from base case[a]							
	Capital investment				Revenue requirements			
Case variations	Untreated	Dravo	IUCS	Chemfix	Untreated	Dravo	IUCS	Chemfix
Plant size	Large	Large	Large	Large	Large	Large	Large	Large
Remaining plant life	Large	Moderate	Slight	Slight	Moderate	Small	Slight	Slight
Ash in coal	Small	Small	Small	Small	Small	Small	Small	Small
Sulfur in coal	Moderate	Small	Small	Small	Small	Moderate	Small	Small
No flyash in sludge	Moderate	Small	Slight	Moderate	Moderate	Moderate	Small	Moderate
Distance to disposal	Large	Large	Small	Large	Large	Large	Large	Large
Fixation additive rate	-	Slight	Slight	Small	-	Small	Slight	Large
Limestone vs lime scrubbing process	Slight	Small	Slight	Slight	Slight	Slight	Slight	Small
Thickened sludge	Small	-	-	-	Small	-	-	-
Thickened sludge and distance to disposal site	Large	-	-	-	Large	-	-	-
Filtered sludge	Large	-	-	-	Small	-	-	-
Filtered sludge and distance to disposal site	Large	-	-	-	Large	-	-	-
Constraint of available pond acreage	Moderate	-	-	-	Moderate	-	-	-
Pond lining	Large	-	-	-	Large	-	-	
Truck to disposal	-	-	-	Small	-	-	-	Slight
Intermediate ponding and truck to landfill	-	Large	-	-	-	Slight	-	-
Settled density in pond	Small	Large	-	-	Small	Large	-	-

a. An arbitrary scale is established with the following rating criteria being applied.
Slight: less than ±10% change from the base case
Small: from ±10% to ±20%
Moderate: from greater than ±20% to ±40%
Large: greater than ± 40%

*Reference 28.

case (1,500 MW existing, 15 year remaining life), the IUCS process was 175 percent more expensive than untreated disposal.

The most important conclusion to be drawn from the TVA work is that commercial fixation can be competitive with untreated FGD sludge disposal in some instances. The actual cost of any disposal alternative is site-specific, so generalizations are not recommended.

Michael Baker, Jr., Inc. (1977)

The Michael Baker study for EPRI evaluated the state-of-the-art of FGD sludge fixation and included detailed cost estimates for untreated sludge disposal (wet and dry), and Dravo and IUCS fixation. This study used a single model plant (similar to the TVA base case) for cost analysis. The results showed that fixation is only slightly more expensive than wet or dry untreated disposal for the model plant. The 30-year levelized revenue requirements for the respective processes were as follows:

Wet disposal without fixation	$10.90
Dry disposal without fixation	$11.00
Dry disposal with fixation (IUCS)	$12.40
Wet disposal with fixation (Dravo)	$14.60

It was noted in the study that the figures are again quite sensitive to site-specific conditions and requirements, in particular, the hauling distance to the disposal site, cost of fixation additives, and site geology. Blanket conclusions about the relative cost of these disposal alternatives were therefore avoided.

Ongoing Studies of FGD Sludge Disposal Economics

SCS Engineers is currently under contract with EPA (No. 68-03-2471) to assess the economic impact of various FGD sludge disposal regulatory scenarios on the utility industry. Using the TVA estimates, a comprehensive list of model plants will be developed and their disposal costs assessed based upon variation in the TVA base case.

Selected regulatory scenarios will then be applied to the model plants to determine the most cost-effective means of industry compliance. Results are expected in late 1978.

TVA is also expanding the previous effort to include costs for: (1) disposal of gypsum from FGD sludge-forced oxidation, and (2) disposal of untreated sludge which is dewatered and blended only with fly ash.

REGULATIONS WHICH IMPACT UPON FGD SLUDGE DISPOSAL

Regulations that have been or could be applied to residual disposal practices fall under one or more of the following classifications:

- Water quality criteria for various beneficial uses;
- Comprehensive air quality criteria;
- Solid waste disposal;
- Industrial and hazardous waste disposal;
- Waste disposal to oceans;
- Waste disposal to mines.

In implementing a residual disposal plan for FGD-equipped power plants, the power companies have had to comply with one or more of the above regulations.

Water Quality Standards

The Federal Water Pollution Control Act Amendments of 1972 (Public Law 92-500) established the framework for the water quality control laws and regulations used by the various states. Under Public Law 92-500, the states retain the primary responsibility for water quality protection. However, the U.S. EPA is authorized to intervene, if the states do not enforce the law. The relevant elements of Public Law 92-500 are:

- Water Quality Standards Program
- NPDES Program
- Treatment Requirements
- Effluent Guidelines

All states currently operate a water quality standards program for surface waters, which is used as a basis for issuance of discharge permits. These water quality standards would only be applicable to FGD sludge liquors if they were discharged to a surface water. The recommended regulating parameters for wastewater disposal include:

- Dissolved oxygen (DO)
- pH and acidity/alkalinity
- Suspended and other particulate solids
- Heavy metals

In nearly all cases, the state regulatory agencies are authorized to protect both surface and subsurface waters, i.e., prevent degradation of groundwater. However, only a few states have specific criteria for groundwater protection.

Air Quality Standards

With the promulgation of the New Source Performance Standards (NSPS) for Fossil Fuel-Fired Steam Generators (40 CFR, Part 466, 8/17/71), wet lime/limestone scrubbers became the anticipated "best method" of removing SO_2 from the flue gas of a power plant.

The NSPS were remanded to EPA by a U.S. Court of Appeals in 1973, with one of the allegations involving insufficient EPA consideration of the sludge disposal problem. The court decision stated that the record be remanded for further "consideration and explanation...of the adverse environmental effects of requiring a 1.2 lb/million (BTU) standard for those... plants which must use a lime slurry scrubbing system..."

In its Response to Remand (40 FR42045) EPA concluded that the standards should not be revised to account for sludge disposal. It was noted, however, that "EPA considers permanent land disposal of raw sludge to be environmentally unsound, because it definitely degrades on large quantities of land" (Section C.I. (c)). As an acceptable solution, both fixation and alternate control systems which do not generate sludge are considered acceptable. The response states that "Fixation of the sludge will greatly reduce its environmental impact," as it has a "much lower leachability" than untreated sludge "and the leachates...are potentially less of a disposal problem than (those) from fly ash."

Subsequent legal decisions (Essex Chemical, Indiana Public Service) have failed to resolve the issue of turning an air pollution problem into a potential water pollution problem. EPA has not as yet stated a formal position on FGD sludge disposal other than that implied in the Remand.

Other Waste Disposal Requirements

Federal regulations controlling the disposal of certain industrial wastes could be applied, at least indirectly, to the disposal of FGD sludges. Similarities between these waste categories and FGD sludges are based on one or more common potentially hazardous constituents and/or a similarity in the method of disposal. The industrial wastes discussed below are:

- Slimes from phosphate mining;
- Acid mine drainage;
- Gypsum from phosphoric acid manufacture; and
- Coal mine tailings.

The principal regulatory emphasis in these industries is toward proper impoundment construction due to a history of catastrophic structural failures. Groundwater protection and physical stabilization are typically not considered in federal or state regulation of disposal of these wastes.

Solid Waste

The predominant method for the ultimate disposal of solid waste is the landfill. Generally, federal and state regulations governing the disposal of solid waste apply typically to specific waste classifications (municipal refuse, brush and tree wastes, demolition and construction waste, sewage sludge, bulky wastes). The regulation of these facilities and activities has been the primary responsibility of state and local agencies.

Federal Mandates--

The recent passage of PL 92-580, the "Resource Conservation and Recovery Act of 1976" (RCRA), sould have some impact on FGD sludge disposal regulation by states. The most applicable portion of RCRA is Subtitle C, "Hazardous Waste Management," under which EPA must develop criteria for listing hazardous wastes. According to RCRA, a hazardous waste is defined as: "a solid waste, or combination of solid wastes, which because of its quantity, concentration, or physical, chemical, or infectious characteristics may -

> (A) cause, or significantly contribute to, an increase in mortality or an increase in serious irreversible, or incapacitating reversible, illness; or
>
> (B) pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed of, or otherwise managed."

Should FGD wastes or any portion thereof meet these criteria, standards promulgated under RCRA for waste transport, treatment, storage, and disposal would become applicable. The hazardous waste "definition" under RCRA is not expected until early 1978.

Section 3001 stipulates that criteria for "identifying the characteristics of hazardous waste, and for listing hazardous waste" shall be promulgated by early 1978. Similarly, standards applicable to generators, transporters, and disposers of hazardous waste shall be promulgated.

State Regulations--

Examination of the solid waste regulations for the 50 states revealed some notation of groundwater protection, flood plain consideration, and site reclamation in almost every case. The degree of specificity varied significantly, however, as many states prefer a permit system and reserve the right to site-specific evaluation.

Many of the power plants employing FGD have been subject to disposal site approval by state solid waste agencies. Site evaluation is usually limited to soils analysis, including permeability and chemical analysis. Contacts with state agencies revealed that FGD site evaluation criteria were generally excerpted from applicable landfill requirements, since specific FGD sludge disposal site evaluation criteria were not available.

Table 9 summarizes the groundwater, flood protection, and site reclamation rules for selected states in which an FGD-equipped utility is presently located; thede do not necessarily reflect the fules which were applied to the FGD systems themselves, but serve only as an interpretation of the written regulations. Those state regulations which do not specifically refer to the given problem are indicated by the word "none." Specific comments follow concerning leachate control, flood and drainage control, and site reclamation.

Leachate from Sludge Disposal--Most states have adopted the federal recommendation for protecting groundwater quality beneath solid waste disposal sites without significant extrapolation. Some, however, have speci-

TABLE 9.*

STATE SOLID WASTE REGULATIONS PERTAINING TO EXISTING FGD SYSTEMS

State	Groundwater	Floods	Rainfall	Reclamation
Ariz.	General protection	None	None	2' minimum cover
Col.	General protection	General rainfall protection	General rainfall protection	
Fla.	Monitoring, possible leachate collection	Away from flood plain	General diversion	2' minimum cover, 33% slope (sides)
Ill.	Monitoring, soil analysis	General rainfall protection	General rainfall protection	2' minimum cover, 50% slope (sides)
Kan.	General protection, soil analysis	None	None	State approval
Ky.	General protection, soil analysis	100 yr. flood	General diversion	2' minimum cover, revegetation
Mo.	Monitoring, soil analysis, possible leachate collection	100 yr. flood	20 yr. rainfall	2' minimum cover, 33% slope (sides) revegetation
Mont.	General protection, soil analysis	100 yr. flood	20 yr. rainfall	2' minimum cover
Nev.	Stabilize or neutralize	None	None	2' minimum cover, 2-4% slope
Penn.	Monitoring, soil analysis, possible leachate collection	50 yr. away from flood plain	General diversion	2' minimum cover, 1-15% slope

*Reference 29

fied restrictions pertinent to site design and location. Most states which require groundwater monitoring during operation of the fill also require the monitoring to be continued for a specified period after closure.

Flooding and Drainage Considerations--Most of the state solid waste disposal regulations address the problem of flooding, while all regulations mention or specify the fill slope necessary to divert runoff water.

Flood consideration varies with each regulation, from simple mention of the potential danger to specifications regarding site location based on flood probability. Most states specify that the site shall not be located within a 50- or 100-yr flood plain. Some require encapsulation or other protection if the site is to be located in a flood plain. Provisions to eliminate standing water from landfills would obviously apply only to stabilized or dried sludge lagoons and landfills.

Provisions for Site Reclamation--The extent to which a landfill site is reclaimed is up to the owner. Many states do, however, require a certain amount of landscaping and planting to prevent devaluation of nearby properties, excessive erosion, or standing water accumulation. Reclaimed site uses vary, but most landfills are developed into recreation areas; the erection of structures over the fill is generally not recommended due to structural instability and subsidence.

Regulating parameters such as load-bearing strength are rarely, if ever, applied to site reclamation. Some states require that subsidence, surface erosion, and cracking be monitored for several years after closure.

SUGGESTED REGULATORY APPROACH(30)

The physical and chemical properties of FGD sludge set a need for regulation. Because the impact of these sludge characteristics on the environment will vary according to certain characteristics of the site, an equitable regulatory approach would be based upon these site characteristics.

The suggested regulatory approach is analogous to the procedures being followed by state regulatory agencies in establishing guidelines and limitations for treated wastewater point sources. Regulatory agencies in their review of proposed new wastewater treatment facilities for point source discharges go through the following steps:

1. The beneficial use of the receiving water is established;
2. Based upon the beneficial use established, maximum concentrations for various contaminants in the treated effluent are set;
3. The applicant responds with a treatment technology which will theoretically supply sufficient treatment to meet the effluent limitations on a sustained basis;
4. Upon approval of the technology, the regulatory agency will provide the applicant with specific design criteria for use in preparing detailed design plans and specifications; and
5. Finally, the regulatory agency establishes monitoring, control, and reporting procedures which the applicant must implement to ensure that the effluent limitations established in No. 2 above are being met.

The above approach is site-specific, as opposed to a universally applied "one number" approach and recognizes that local site conditions are important in establishing best practical control technology. The approach also provides continuous interaction between applicant and regulatory agency to ensure that environmental protection objectives are met.

The wastewater effluent limitations approach outlined above can be adopted to FGD sludge treatment/disposal guidelines and limitations. Figure 1 shows in a simplified flow diagram the major steps involved. If each of the steps shown can be carefully defined in a procedural manner, it will provide a uniform, organized approach to decision-making based upon site/waste-specific data. The following is a discussion of each of these steps:

Define Beneficial Uses

In this step, the regulatory agency, with the cooperation of the applicant, performs an evaluation of the proposed disposal site to determine what beneficial environmental resources require protection. The environmental factors which warrant

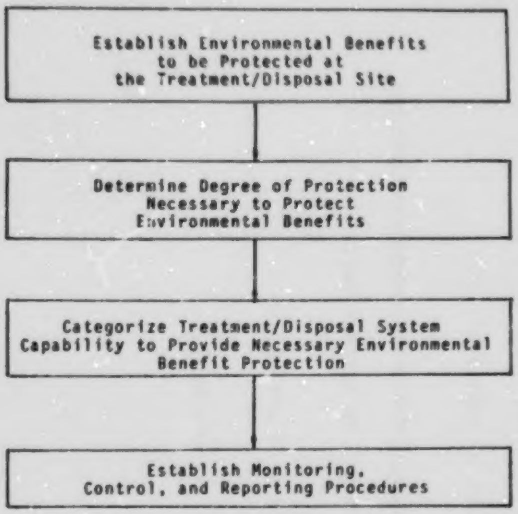
Establish Environmental Benefits to be Protected at the Treatment/Disposal Site
Determine Degree of Protection Necessary to Protect Environmental Benefits
Categorize Treatment/Disposal System Capability to Provide Necessary Environmental Benefit Protection
Establish Monitoring, Control, and Reporting Procedures

FIGURE 1.* STEPWISE APPROACH TO THE PROPOSED REGULATORY SYSTEM

*Reference 30

protection during FGD sludge disposal are the following:

1. Groundwater resources underlying the site;
2. Local surface water resources at elevations lower than the site; and
3. Future land uses at the site location.

In order to characterize the groundwater resources, a detailed hydrological report would be required. The report would include: (1) the location and size of groundwater aquifers, (2) the quality of each aquifer, and (3) a best estimate of the existing and/or potential beneficial uses of each aquifer.

The potential dangers to local surface waters should be evaluated. This assessment would be based on the following criteria:

- Distance from site to surface water(s);
- Elevation difference between site and surface water(s);
- Type of surface water(s), e.g., lake, river, etc.;
- Present or projected beneficial uses of surface water(s); and
- Volume and/or flow rate(s) of the surface water.

Future land use would be projected to some point in time to determine the extent of site reclamation required. The load bearing capability of ponded, unstabilized sludge is generally poor. With proper cover material, light recreational use is possible, but in essence the pond area is eliminated from higher use purposes. However, in some disposal site areas this situation may be acceptable, because the land has little projected value.

Categorize Sites According to Degree of Protection Necessary

Having assessed the acceptability of the site for FGD sludge disposal, the site can then be categorized for the purpose of regulation. Table 10 lists 7 comprehensive site categories based upon possible beneficial uses. The categories range from sites having no environmental benefits to protect (Category 1), to sites which are unacceptable for FGD sludge disposal because no practical technique will adequately protect a valuable groundwater resource.

The 7 categories selected evolved from the various combinations of decisions which would be made based on each site variable. In order to better demonstrate the logic of site categorization, Figure 2 shows a conceptual decision tree approach. Each of the decision points is based on the following 5 variables:

1. Possible future land use
    - possible urban or industrial development
    - little or no probability of development
2. Groundwater resources
    - potentially useful
    - do not meet useful standards or not accessible for use
3. Protection of groundwater by site
    - time constants (rate of flow)
    - rate constants (mass transport of contaminants)
4. Surface water protection
    - sludges cannot reach water course

TABLE 10. PROPOSED CATEGORIZATION OF FGC DISPOSAL SITES

Site Category No.		Environmental Benefit Requiring Protection		Protection Method		Site Modification - Reduce Mass Transport
	Land Value	Surface Water	Groundwater	Sludge Pretreatment	Retention Dikes	
1	Low	No	No	No	Standard	No
2	Low	Yes	No	No	Extraordinary(2)	No
3	High	No	No	Stabilize(1)	Standard	No
4	High	No	Yes(3)	Stabilize	Standard	Yes
5	Low	No	Yes	No	Standard	Yes
6	Low	Yes	Yes	No	Extraordinary	Yes
7	Site unacceptable regardless of protection methods used due to impossibility of adequately protecting groundwater resource					

(1) It is assumed that stabilized sludge will not flow and poses no threat to surface water regardless of retention dike integrity.

(2) Dual dikes, supplementary interceptor pond, or other failsafe method of preventing escape of sludge if primary dikes fail.

(3) See narrative for discussion of pollutant mass transfer potential through soil.

*Reference 30.

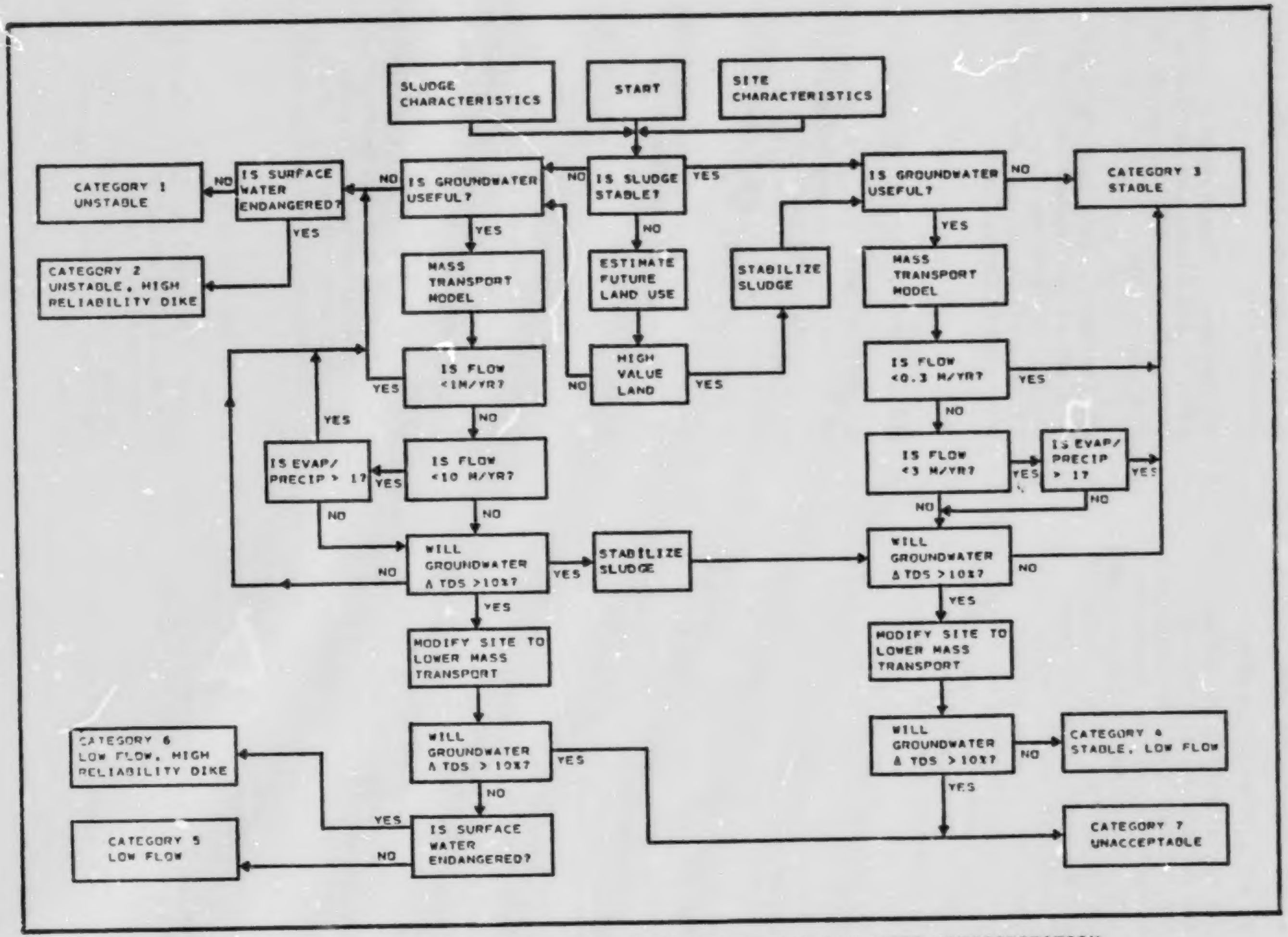
SLUDGE CHARACTERISTICS
START
SITE CHARACTERISTICS
IS SLUDGE STABLE?
IS GROUNDWATER USEFUL?
IS SURFACE WATER ENDANGERED?
CATEGORY 1 UNSTABLE
CATEGORY 2 UNSTABLE, HIGH RELIABILITY DIKE
MASS TRANSPORT MODEL
IS FLOW <1M/YR?
IS FLOW <10 M/YR?
IS EVAP/PRECIP > 1?
WILL GROUNDWATER Δ TDS >10%?
MODIFY SITE TO LOWER MASS TRANSPORT
WILL GROUNDWATER Δ TDS > 10%?
IS SURFACE WATER ENDANGERED?
CATEGORY 6 LOW FLOW, HIGH RELIABILITY DIKE
CATEGORY 5 LOW FLOW
ESTIMATE FUTURE LAND USE
HIGH VALUE LAND
STABILIZE SLUDGE
STABILIZE SLUDGE
IS GROUNDWATER USEFUL?
CATEGORY 3 STABLE
MASS TRANSPORT MODEL
IS FLOW <0.3 M/YR?
IS FLOW <3 M/YR?
IS EVAP/PRECIP > 1?
WILL GROUNDWATER Δ TDS >10%?
MODIFY SITE TO LOWER MASS TRANSPORT
WILL GROUNDWATER Δ TDS >10%?
CATEGORY 4 STABLE, LOW FLOW
CATEGORY 7 UNACCEPTABLE
YES
NO

FIGURE 2.* DECISION TREE APPROACH TO DISPOSAL SITE CATEGORIZATION

*Reference 30

- sludges can reach water course

5. Site meteorology
   - Net evaporation area
   - Net precipitation area

The rationale for selecting the values shown and the related alternatives is partially subjective. Zero impurity transport is physically impossible, but acceptable mobility limits (mass transport) have not been legally defined. Also, levels of "acceptable degradation" have not been defined. Thirdly, the prediction of land use (and value) has not been defined legally or socially. Recognizing these constraints, the categorization approach is nonetheless valid in concept based upon the existing data base for FGD sludge disposal.

Establish Monitoring, Control, and Reporting Procedures

Once the disposal site had been subjected to the above criteria, it would become operational under the appropriate category and its restrictions. Monitoring, control, and reporting procedures should be specified for all FGD sludge disposal sites.

During the categorization procedure, the potential for environmental impact from several parameters was evaluated. These parameters included:

- Groundwater contamination
- Sludge in-place stability
- Catastrophic sludge release to surface waters

The monitoring system would be established for each of the above parameters to verify, on a continuing basis, the validity of the categorization scheme selected.

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LABORATORY CHARACTERIZATION OF THE THERMAL DECOMPOSITION OF HAZARDOUS WASTES

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ABSTRACT

A specialized laboratory system incorporating a two-stage quartz tube was utilized for determining the thermal destruction properties of pesticides and other hazardous organic substances. With this system, a small sample was first converted to the gas phase, then exposed to high-temperature destruction conditions in flowing air. Critical parameters of temperature and residence time were accurately measured. High-temperature decompositions of Kepone, Mirex, DDT, and PCB's have been studied.

At this time, a new, more sophisticated closed system is being developed to conduct thermal destruction studies. In addition to increased versatility and more refined control of the thermal destruction process, a gas chromatograph-mass spectrometer with dedicated minicomputer is being coupled to the system as a tool for identifying and quantifying products of decomposition.

INTRODUCTION

The problems associated with the safe disposal of hazardous organic waste materials have been recognized for several years. For these materials, high temperature incineration is being considered as a method of permanent disposal. However, there is a serious lack of basic data concerning the high-temperature decomposition behavior of organic materials.

On the laboratory-scale, accurate measurements can be obtained of destruction temperature and residence time. In addition, thorough analysis of the decomposition and/or recombination products will definitely show if controlled high-temperature incineration is a viable disposal route for a specific waste material. Consequently, such laboratory-scale testing should logically precede pilot-scale studies and the eventual use of full-size hazardous waste incinerators.

The University of Dayton Research Institute, operating under Environmental Protection Agency grants, is developing laboratory procedures for studying the high-temperature decomposition of a wide variety of organic hazardous waste materials. The purpose of this presentation is to discuss the laboratory instrumentation and to describe its practical application.

RATIONALE OF LABORATORY APPROACH

In order to determine the high-temperature destruction characteristics of an organic molecule, it is necessary to obtain precise information on certain crucial parameters. It is important that the exposure temperature be accurately determined, along with the residence time, i.e., the time interval during which the molecule experiences the destructive temperature. Another critical parameter that must be fulfilled in such an evaluation is that there be an adequate supply of air so that the destruction takes place in an oxidative environment, as opposed to an atmosphere containing insufficient oxygen. Lastly, an important factor is the composition of the high-temperature environment, e.g., water content, presence of other gases, and interfering solid materials.

The laboratory approach to establishing a material's high temperature, nonflame destruction characteristics has certain distinct advantages. First, one can examine the undiluted sample without interferences from other materials. Second, the composition of the high-temperature environment can be precisely established by using compressed air of known quality and employing in-line filters to remove water, oil, and other foreign materials. Next, by using a technique whereby a small sample is gradually vaporized and then passed through a high-temperature zone, an excess of oxygen is assured, thus avoiding the possibility of an oxygen-deficient reaction occurring. Further, it is possible to evaluate the behavior of the pure sample on the molecular level. By vaporizing the sample prior to its exposure to the high-temperature environment, one can be assured, based on the kinetic theory of gases(1), that the molecules experience the actual average temperature. Finally, the laboratory evaluation of a sample's destruction characteristics can be accomplished quickly and economically with minimum environmental risk.

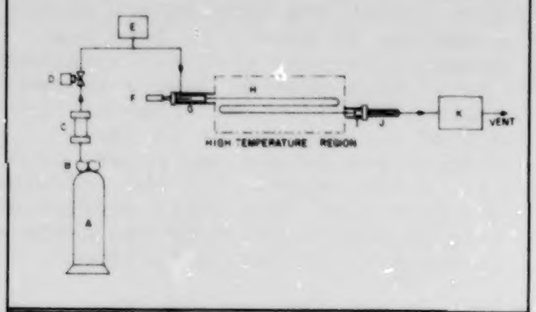
It is important to note that during incineration of waste materials, a certain amount of energy must be applied just to change the organic compounds from their usual state (whether it be solid or liquid) to the gas phase. These phase transitions, apart from requiring additional energy, also require an undefined amount of exposure time to the high-temperature source. Therefore, it is almost certain that in the case of waste materials, some molecules do not encounter the prescribed incineration temperature. In short, even though the temperature within a chamber is known, it does not necessarily mean that all substances within that chamber have attained thermal equilibrium. However, if all of the substances in the chamber are in the gas phase, one can safely assume that the individual molecules have (with sufficient time exposure) achieved the average temperature of that environment.

For similar reasons, the laboratory evaluation of a sample's residence time is considerably simplified over that of measuring residence time in a large scale unit. When a gas is passed through a long narrow-bore flow path (in the laminar flow region), radial dispersion can be neglected and the main factor affecting the residence time distribution is longitudinal dispersion. However, for flow paths that are of large diameter, mixing chamber, or multichamber configuration, radial dispersion is the major factor affecting the variation in residence time of transported molecules.

The approach for obtaining high-temperature destruction data on selected organic wastes utilized a discontinuous system where the thermal stressing of the sample and product analysis were performed separately. Using this approach, various organic samples have been evaluated in a series of tests where the sample was first vaporized and then transported through a narrrow-bore, high-temperature zone by a controlled flow of air. In this way, average temperature and residence time were firmly established. These tests were conducted at a series of temperatures ranging from ∿300°C to 1000°C. Also, the effluent from each high-temperature test was passed through an appropriate trapping medium and the collected fraction was subsequently analyzed by gas chromatography.

Quartz Tube Apparatus

Figure 1 is a schematic of the high-temperature quartz tube



A	COMPRESSED AIR, BREATHING QUALITY GRADE
B	TWO STAGE PRESSURE REGULATOR
C	"HYDROPURGE" FILTER
D	FLOW CONTROL VALVE
E	PRESSURE TRANSDUCER
F	SAMPLE HOLDER, PYREX
G	HEATED INLET CHAMBER
H	QUARTZ TUBE
I	HEATED OUTLET CHAMBER
J	EFFLUENT TRAP, TENAX-GC OR CHARCOAL
K	FLOW METER

Figure 1. Schematic of Quartz Tube Apparatus.

apparatus that was designed and assembled for the examination of pesticides and other organic wastes.

Upstream of a folded quartz tube, in a furnace capable of 1000°C is a special sample holder. With the use of a 10 microliter syringe, a known quantity of sample can be readily deposited on the sand blasted region of the sample holder. The solvent quickly evaporates, leaving the pure sample on the rough Pyrex surface. This device is then inserted into a chamber upstream of the high temperature quartz tube. Next, this chamber is heated to vaporize the pesticide or other organic waste. The gas phase sample is then swept through the high-temperature tube, and captured in an effluent trap located at its outlet. The outlet of the trapping medium tube is near ambient temperature. Once the sample molecules, or fragments and products thereof, have passed through the high-temperature quartz tube, they are trapped in, or on, the sorbing medium of the effluent trap. This trap is then removed from the high-temperature apparatus, and a quantitative standard deposited in the trap (4.0 μg of n - octadecane in a 50:50 vol mixture of acetone and benzene). The contents are then subjected to a programmed temperature gas chromatographic analysis using a modified Tracor 550 Instrument (Figure 2).

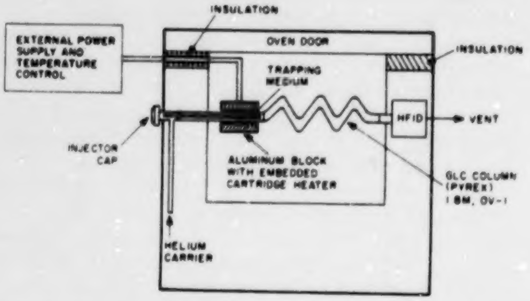

INSULATION
EXTERNAL POWER SUPPLY AND TEMPERATURE CONTROL
OVEN DOOR
INSULATION
TRAPPING MEDIUM
HFID
VENT
INJECTOR CAP
ALUMINUM BLOCK WITH EMBEDDED CARTRIDGE HEATER
GLC COLUMN (PYREX) 1.8M, OV-1
HELIUM CARRIER

Figure 2. Interior of Modified Tracor 550.

During this study, different trapping media were investigated. Of these, Tenax-GC was found to be an excellent trapping medium for the three pesticides and their large fragmentation products. Tenax-GC, a porous polymer, is currently commercially available in 35/60 and 60/80 mesh sizes, and possesses a desirable feature in that it can be readily, thermally desorbed(2-6). Traps prepared with the 60/80 mesh Tenax-GC particles performed quite well and did not present an excessive pressure drop. Also, a 2.0 cm length of Tenax-GC was sufficient to obtain quantitative recoveries of the pesticides. However, acetone and benzene were not quantitatively retained at the typical trap inlet temperature of approximately 300°C.

Discussion

To illustrate the success achieved with the system, a brief review of the work done with Kepone, Mirex, and DDT follows. The chemical structures of these compounds are shown in Figure 3.

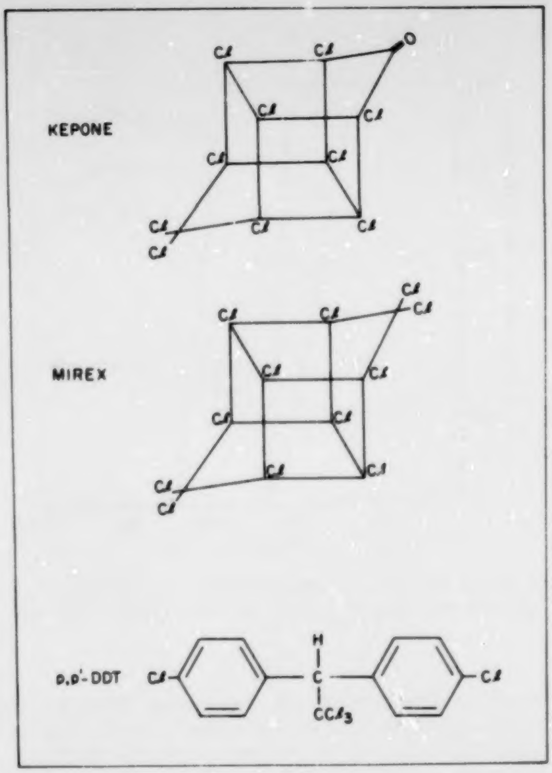


Figure 3. Chemical Structures.

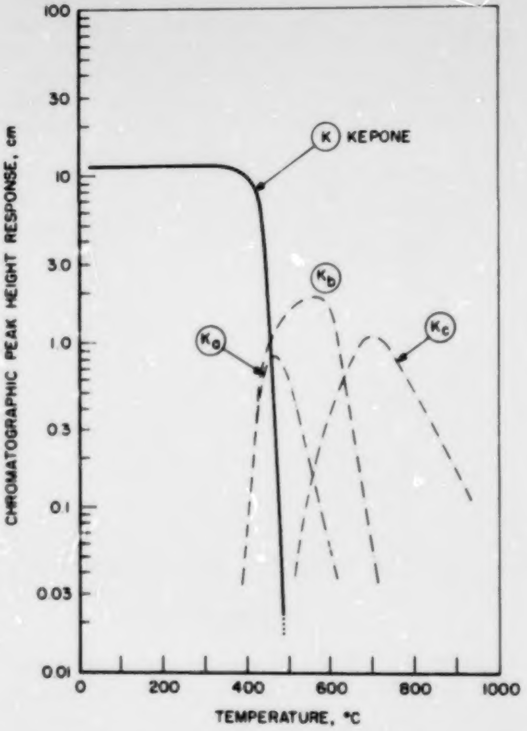


Figure 4. Thermal Destruction Plot for Kepone.

Destruction of Kepone

From the present experimental data, it was observed that Kepone can be readily vaporized in flowing air at temperatures ranging from approximately 200° to 300°C. It was also observed that this temperature range is not destructive to the Kepone molecule. However, when Kepone was subjected to temperature above 350°C, decomposition does occur as is evidenced by the rapid drop in the Kepone concentration shown in Figure 4. Also, it is seen that the thermal degradation of Kepone at exposure temperatures less than 600°C is markedly different from that when gaseous Kepone is subjected to a temperature exceeding 600°C. For example, peak K_a, which was identified as hexachlorocyclopentadiene, was formed at temperatures below 500°C; however, it was not found above 600°C. Conversely, K_c, which was determined to be hexachlorobenzene, was observed only in the products of tests conducted above 600°C. K_b was not identified.

Effect of Residence Time

The thermal breakdown of Kepone is pronounced in the 420° to 440°C region. Consequently, this temperature region was selected for an experimental evaluation of the effect of residence time on the destruction of Kepone. Accordingly, three separate tests were conducted with 40 μg samples of Kepone at a carefully controlled $\bar{T}_2$ of 433°C. The first test was conducted with a residence time, t_r, of 1.79 sec. The t_r for the second test was 1.04 sec, while for the third test, t_r was 0.23 sec. These different residence times were obtained by appropriately adjusting the air flow control valve of the quartz tube apparatus. Chromatograms were obtained from the captured effluents. From these chromatographic data, the concentrations of emerging Kepone were plotted versus residence time, as shown in Figure 5. It is evident from this logarithmic plot that residence time is a strong factor in the destruction of Kepone at 433°C.

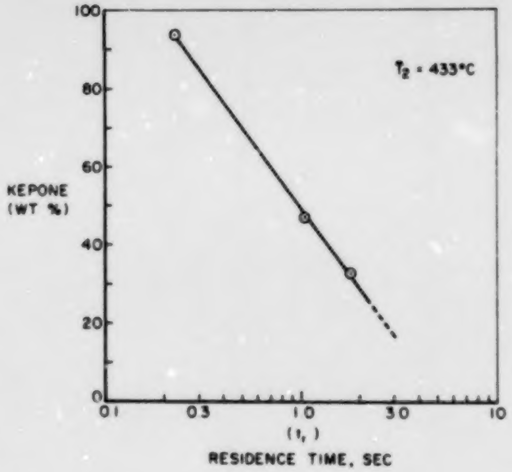


Figure 5. Effect of Residence Time on Thermal Destruction of Kepone.

Comparison of the Three Pesticides

Studies similar to that done with Kepone were performed with Mirex and DDT. From compiled GC data, thermal destruction plots were prepared for Kepone, Mirex, and DDT. Figure 6 shows a direct comparison of the high-temperature destruction of the three pesticides. Mirex is the most thermally stable of these three, with Kepone next, and DDT the least stable.

Current Work

Past work at the University of Dayton Research Institute$^{(7,8)}$ has confirmed that there is a definite destruction temperature/residence time relationship in a nonflame mode when an organic compound is subjected to an oxidative thermal exposure. It follows then that any system designed to evaluate destruction characteristics must have the capability of precise control and measurement of these important parameters.

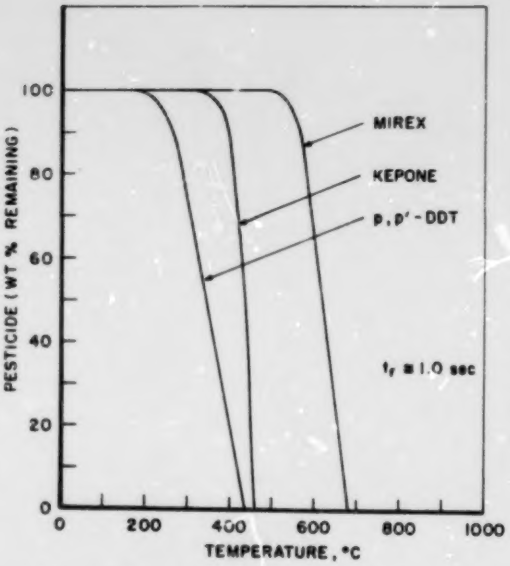


Figure 6. Comparison of Thermal Destruction of the Three Pesticides.

The new system now being developed will employ a two-stage destruction setup, similar to that used in our earlier work. However, a major improvement in the handling and analysis of the decomposition products will be accomplished by incorporating into the system a gas chromatograph-mass spectrometer-data system (GC-MS-DS) as shown in Figure 7.

As can be seen from the block diagram, the in-line system is closed; therefore, a complete capture and subsequent analysis of evolved products can be achieved. The gas chromatograph shown just upstream of the mass spectrometer must of necessity be a complex separatory device in order to resolve individual compounds from the wide range of expected decomposition products. High resolution gas chromatography, employing glass open tubular columns, will be used to

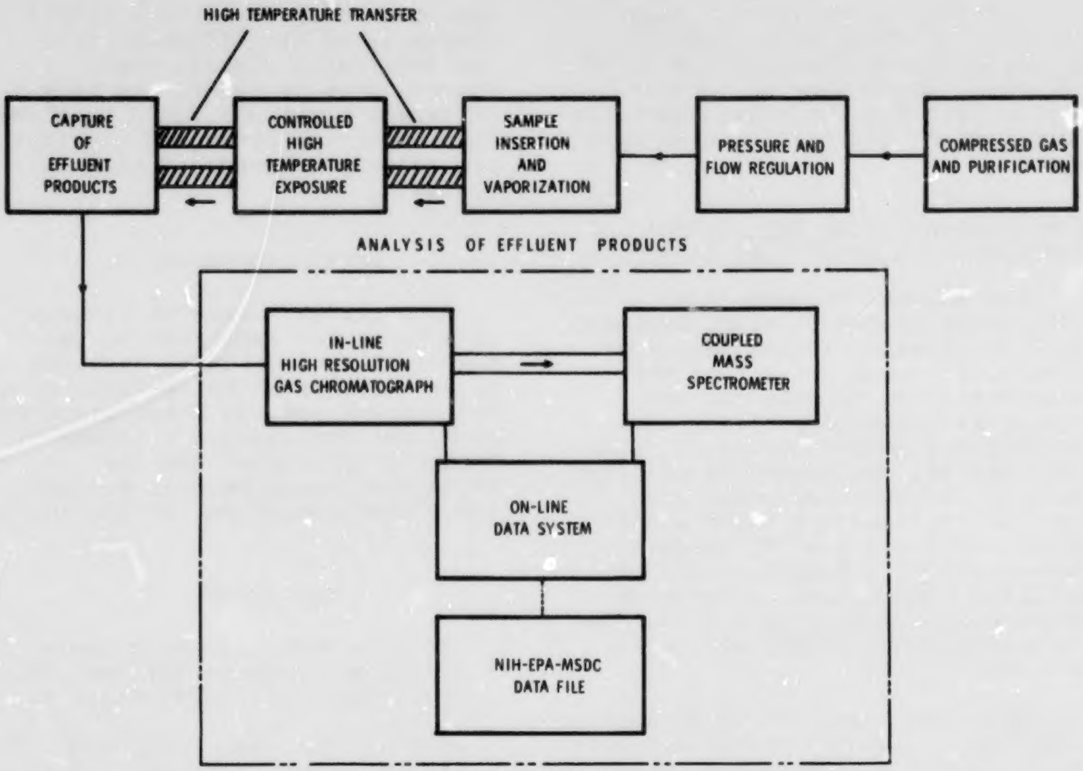

HIGH TEMPERATURE TRANSFER
CAPTURE OF EFFLUENT PRODUCTS
CONTROLLED HIGH TEMPERATURE EXPOSURE
SAMPLE INSERTION AND VAPORIZATION
PRESSURE AND FLOW REGULATION
COMPRESSED GAS AND PURIFICATION
ANALYSIS OF EFFLUENT PRODUCTS
IN-LINE HIGH RESOLUTION GAS CHROMATOGRAPH
COUPLED MASS SPECTROMETER
ON-LINE DATA SYSTEM
NIH-EPA-MSDC DATA FILE

Figure 7. Thermal Decomposition Analytical System.

separate and analyze even the trace level components present in the effluent. The mass spectrometer utilizes signals from an electron impact source and will enhance the overall analytical sensitivity of the system as well as the overall detectability of the various decomposition products. The GC-MS is interfaced with a dedicated minicomputer which gathers, processes, and stores the vast quantity of data generated.

With the nonflame version of this system, both residence time and exposure temperature can be precisely controlled. Specifically, the residence time is determined by accurately measuring the internal pressure, temperature, and the gas-volume throughput for a narrow-bore quartz tube(8). The exposure temperature is determined by measuring the average ambient temperature that surrounds the quartz tube. Again, with this new system, product analysis will serve as the basis for evaluating the degree of destruction of the hazardous wastes at the different exposure temperatures and residence times.

In our earlier program, the prime objective was to determine destruction temperature/residence time conditions for pesticide molecules. However, along with the parent pesticide analyses, a limited search and identification was made of various decomposition and recombination products which were heavier than ∿150 molecular weight. In some of our thermal destruction tests, particularly at intermediate temperatures, substances of higher toxicity than the parent molecule have been formed. Consequently, with the new system, the entire range of decomposition products will be captured and analyzed. This complete spectrum of a sample's decomposition products could be of paramount importance to parties responsible for the environmentally-safe thermal disposal of hazardous wastes.

Characteristics of the Thermal Decomposition Analytical System

The thermal decomposition analytical system is being designed with two distinguishing features: flexibility with respect to the test variables of interest and "quick-response" capability when results are needed promptly. With this system, the gathering of basic data can be obtained under controlled conditions in both a non-flame and flame mode of thermal decomposition. However, with the built-in flexibility, parameters which can be easily varied can also be well controlled and accurately measured.

There are numerous advantages in adopting the closed system approach. First, the closed system permits the total collection of decomposition products. Also, the analytical data acquisition can be accomplished with a minimum of error, as the systematic errors generally associated with sample handling in a discontinuous technique will be eliminated. Additionally, this thermal decomposition analytical system can be applied to a wide range of organic hazardous materials. The system will have the capability to examine such samples as fire retardants, agricultural chemicals, industrial wastes, environmental contaminants, and a wide variety of other organic waste materials. It will be capable of handling liquid, solid, gaseous, and polymeric organic materials.

The expansion of analytical capabilities with the new system will allow a gathering of information that was not previously available. For example, the effluent resulting from a high-temperature gas phase destruction of a multi-component organic mixture would be expected to differ from a simple composite of the effluents from the individual constituents. Indeed, in some cases, entirely different compounds would be formed. Such important synergistic effects can readily be examined with this system.

ACKNOWLEDGEMENTS

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STANDARDIZED METHODS FOR SAMPLING AND ANALYSIS OF HAZARDOUS WASTES

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ABSTRACT

The management and regulation of hazardous wastes must be based on a sound knowledge of waste compositions. The complexity and diversity of industrial wastes necessitate the availability of specialized sampling and analytical procedures. Methods have been developed for safe, reproducible, and representative sampling of such wastes in a wide variety of physical states, compositions, and locations.

Analysis of wastes has been developed as a four level scheme, which begins with field characterization, followed by three levels of progressively more detailed and instrument intensive laboratory analysis. Each level is designed to serve a particular informational need of a waste management or regulatory program. The first laboratory level is designed to give rapid information on the general nature of waste composition and hazardous properties. The second level consists of more detailed but qualitative procedures for both inorganic and organic components. The third level is designed to give a more complete set of quantitative data.

Methods for sampling, containment, handling and custody of waste samples as well as the individual analytical procedures and the rationale for using an analytical scheme will be discussed.

INTRODUCTION

The proper management of, regulation of, or resource recovery from industrial wastes is not possible without an adequate knowledge of the physical and chemical characteristics of the waste. This information comes from a detailed examination of the waste producing process, or of the waste itself. In either case, techniques are required for sampling and analysis of such wastes. As mixtures become more and more complex in physical and chemical characteristics, the problems of representative sampling and of analysis increase dramatically.

Under a 1972 Industrial Waste Control Act, the California Department of Health (CDH) initiated a Hazardous Waste Management Program in late 1973. By mid 1974, a chemical support unit was formed to address the problems of what were hazardous industrial wastes in all of their diversities. Almost immediately it became clear that existing methods of chemical sampling and analysis were inadequate for this purpose. Many specialized sampling methods were practiced in various industry segments designed to meet the problem of specific product lines. In such situations, the compositions are relatively known, and constant which result in greatly simplified sampling and analytical problems. Additionally, much has been published on sampling and analysis of water and wastewater. Such procedures are designed primarily for relative homogeneous, dilute aqueous media and are either inapplicable or used with great difficulty with industrial wastes.

When the National Resource Conservation and Recovery Act (PL 94-580) was passed in October 1976, the law mandated the U.S. Environmental Protection Agency (EPA) to initiate a program to identify and list hazardous wastes and criteria. One of the needs for EPA to initiate the program was the development of methodology for the sampling of hazardous wastes. The EPA awarded the California Department of Health a research grant to assist in this effort.

Under this grant, the CDH embarked on a study to develop a handbook for sampling hazardous wastes. The study was based on some initial procedures and equipment designs developed in field operations conducted by the CDH and a literature search.

The guidelines used in choosing the candidate procedures were the commercial availability of the sampling equipment, cost, simplicity in design and resistivity to chemical reactions. The samplers should be available in commercial supply houses, or readily constructed and inexpensive enough to be discarded when not easily cleaned or decontaminated.

The candidate methods and samplers were subjected to laboratory and field tests. The laboratory tests consisted of sampling water with the liquid samplers. The samplers were then observed for leakage and ease of transfer of the collected samples. The samplers that passed the preliminary screening were further tested using multiphase liquid mixtures such as water, used motor oil and insoluble sludges. In the field tests, the liquid and solid wastes samplers were tested by sampling actual wastes in various types of containers.

A workable scheme for analysis of hazardous waste must follow the sampling program. Analysis of such wastes presents the problem that complete analysis of most hazardous waste may be so expensive and time consuming as to be impractical, whereas superficial general waste characteristics may not be adequate for proper management decisions. Consequently, a multi-level analytical scheme has been proposed with each level, progressively more detailed and quantitative in scope. Use of each level is keyed to informational objectives of the analysis.

The analytical part of this project is in its developmental phase and far from complete. However, the analytical scheme and several procedural elements of the scheme will be presented.

SAMPLING

PURPOSES AND GENERAL CONSIDERATIONS

Sampling of hazardous wastes is conducted for different purposes. In many instances, it is performed to determine compliance with existing regulations promulgated by the different regulatory agencies. In some cases it is conducted to obtain data for purposes of classifying, treating, recovering, recycling or determining compatibility characteristics of the wastes. Sampling is also conducted as an important part of research activities.

In general, sampling of hazardous wastes requires the collection of adequate and representative samples of the body of wastes. Sampling situations vary so widely that no universal sampling procedure can be recommended. Rather, several procedures are outlined for sampling different types of wastes in various states and containers.

These procedures require a plan of action to maximize safety of sampling personnel, minimize sampling time and cost, reduce errors in sampling and protect the integrity of the samples after sampling. The following steps are essential in this plan of action:

1. Determine what should be sampled
2. Select the proper sampler
3. Design the proper sample container and closure
4. Design an adequate sampling plan which includes the following:
   a) Choice of the proper sampling point
   b) Determination of the number of samples to be taken
   c) Determination of the volumes of samples to be taken
5. Observe proper sampling precautions
6. Handle samples properly
7. Identify samples and protect from tampering
8. Record all sample information in

a field notebook

9. Fill out chain of custody record
10. Fill out the sample analysis request sheet
11. Deliver or ship the samples to the laboratory for analysis.

BACKGROUND INFORMATION ABOUT THE WASTE

Accurate background information about the waste to be sampled is very important in planning any sampling activity. The information is used to determine the types of protective sampling equipment to be used and sampling precautions to be observed as well as the types of samplers, sample containers, container closures, and preservatives (when needed) required. Generally the information about the waste determines the kind of sampling scheme to be used.

Most often, the information about the waste is incomplete. In these instances, as much information as possible must be obtained by examining any documentation pertaining to the wastes such as the hauler's manifest (i.e. Figure 1). When documentation is not available, information may be obtained from the generator, hauler, disposer or processor. The information obtained is checked for hazardous properties against standard reference sources by field personnel.

SELECTION OF SAMPLER

Hazardous wastes are usually complex multiphase mixtures of liquids, semisolids or sludges or solids. The liquid and semisolid mixtures vary greatly in viscosity, corrosivity, volatibility, explosivity or flammability. The solid wastes can range from powders to granules to big lumps. The wastes are contained in drums, barrels, sacks, bins, vacuum trucks, ponds and other containers. No single type of sampler can therefore be used to collect representative samples of the different types of wastes. Table 1 lists most waste types and the corresponding recommended samplers to be used.

CONTAINERS

The most important factors to consider when choosing containers for hazardous waste samples are compatibility, resistance to breakage and volume. Containers must not melt, rupture or leak due to chemical reactions with constituents of waste samples. It is, therefore, important to have some idea of the components of the waste. The containers must have adequate wall thickness to withstand ordinary handling during sample collection and transport to the laboratory. Containers with wide mouths are desirable to facilitate transfer of samples from samplers into the containers. Also, the containers must have enough capacity to contain the required volumes of sample or the entire volumes of samples contained in sample s. Table 2 indicates the choice of containers available and their usage.

SAMPLING PRECAUTIONS AND PROTECTIVE GEAR

Proper safety precautions must always be observed when sampling hazardous wastes. In all cases a person collecting a sample must be aware that the waste can be a strong sensitizer, corrosive, flammable, explosive, toxic and capable of releasing extremely poisonous gases. The background information about the waste should be helpful in deciding the extent of sampling safety precautions to be observed and in the choice of protective equipment to be used.

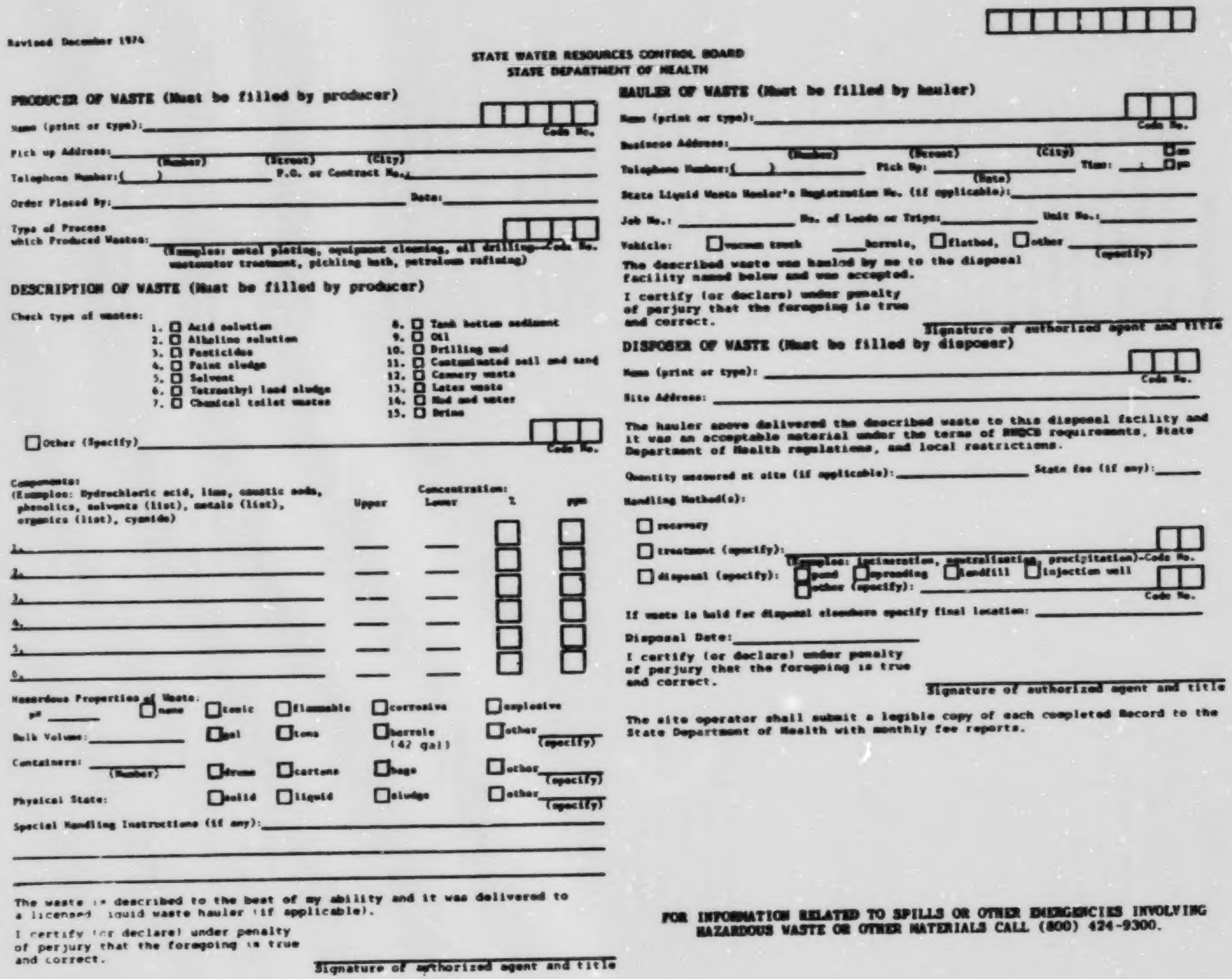
For full protection, the person collecting the sample must use a self-contained breathing apparatus, protective clothing, hard hat, neoprene rubber gloves, goggles and rubber boots.

A self-contained breathing apparatus consists of an air-tight face mask and a supply of air in pressure tank which is equipped with a pressure regulator. Protective clothing consists of long-sleeved neoprene rubber coat and pants, or long-sleeved coverall and oil-and-acid proof apron. In hot weather, the coverall-apron combination might be preferable. Table 3 lists respiratory protective devices and their usage. All equipment, except the respirator, must be properly decontaminated and washed between uses.

SAMPLING EQUIPMENT

Sampling of hazardous wastes requires several different types of samplers. Some sampling equipment is commercially available, while others must be fabricated. This report will cover only the composite liquid waste sampler in detail. Discussions of the soil samplers, grain and other samplers as well as pond and storage tank

FIGURE 1. CALIFORNIA LIQUID WASTE HAULER RECORD



☐☐☐☐☐☐☐☐☐

Revised December 1974

STATE WATER RESOURCES CONTROL BOARD
STATE DEPARTMENT OF HEALTH

PRODUCER OF WASTE (Must be filled by producer)

Name (print or type): ______ ☐☐☐☐☐ Code No.

Pick up Address: ______ (Number) (Street) (City)

Telephone Number: ( ) ______ P.O. or Contract No.: ______

Order Placed By: ______ Date: ______

Type of Process which Produced Wastes: ______ ☐☐☐☐ Code No.
(Examples: metal plating, equipment cleaning, oil drilling, wastewater treatment, pickling bath, petroleum refining)

DESCRIPTION OF WASTE (Must be filled by producer)

Check type of wastes:

1. ☐ Acid solution
2. ☐ Alkaline solution
3. ☐ Pesticides
4. ☐ Paint sludge
5. ☐ Solvent
6. ☐ Tetraethyl lead sludge
7. ☐ Chemical toilet wastes
8. ☐ Tank bottom sediment
9. ☐ Oil
10. ☐ Drilling mud
11. ☐ Contaminated soil and sand
12. ☐ Cannery waste
13. ☐ Latex waste
14. ☐ Mud and water
15. ☐ Brine

☐ Other (Specify) ______ ☐☐☐ Code No.

Components:
(Examples: Hydrochloric acid, lime, caustic soda, phenolics, solvents (list), metals (list), organics (list), cyanide)

Components	Concentration: Upper	Lower	%	ppm
1. ______	___	___	☐	☐
2. ______	___	___	☐	☐
3. ______	___	___	☐	☐
4. ______	___	___	☐	☐
5. ______	___	___	☐	☐
6. ______	___	___	☐	☐

Hazardous Properties of Waste: pH ______ ☐ none ☐ toxic ☐ flammable ☐ corrosive ☐ explosive

Bulk Volume: ______ ☐ gal ☐ tons ☐ barrels (42 gal) ☐ other ______ (specify)

Containers: ______ (Number) ☐ drums ☐ cartons ☐ bags ☐ other ______ (specify)

Physical State: ☐ solid ☐ liquid ☐ sludge ☐ other ______ (specify)

Special Handling Instructions (if any): ______

The waste is described to the best of my ability and it was delivered to a licensed liquid waste hauler (if applicable).

I certify (or declare) under penalty of perjury that the foregoing is true and correct.

______
Signature of authorized agent and title

HAULER OF WASTE (Must be filled by hauler)

Name (print or type): ______ ☐☐☐ Code No.

Business Address: ______ (Number) (Street) (City)

Telephone Number: ( ) ______ Pick Up: ______ (Date) Time: __:__ ☐ am ☐ pm

State Liquid Waste Hauler's Registration No. (if applicable): ______

Job No.: ______ No. of Loads or Trips: ______ Unit No.: ______

Vehicle: ☐ vacuum truck ____ barrels, ☐ flatbed, ☐ other ______ (specify)

The described waste was hauled by me to the disposal facility named below and was accepted.

I certify (or declare) under penalty of perjury that the foregoing is true and correct.

______
Signature of authorized agent and title

DISPOSER OF WASTE (Must be filled by disposer)

Name (print or type): ______ ☐☐☐ Code No.

Site Address: ______

The hauler above delivered the described waste to this disposal facility and it was an acceptable material under the terms of RWQCB requirements, State Department of Health regulations, and local restrictions.

Quantity measured at site (if applicable): ______ State fee (if any): ______

Handling Method(s):

☐ recovery

☐ treatment (specify): ______ ☐☐
(Examples: incineration, neutralization, precipitation)-Code No.

☐ disposal (specify): ☐ pond ☐ spreading ☐ landfill ☐ injection well
☐ other (specify): ______ ☐☐ Code No.

If waste is held for disposal elsewhere specify final location: ______

Disposal Date: ______

I certify (or declare) under penalty of perjury that the foregoing is true and correct.

______
Signature of authorized agent and title

The site operator shall submit a legible copy of each completed Record to the State Department of Health with monthly fee reports.

FOR INFORMATION RELATED TO SPILLS OR OTHER EMERGENCIES INVOLVING HAZARDOUS WASTE OR OTHER MATERIALS CALL (800) 424-9300.

TABLE 1. CHOICE OF SAMPLERS

Waste Type	Sampler	Limitations
Liquids, sludges and slurries in drums, vacuum trucks, barrels and similar containers	Coliwasa a) Plastic	Not for containers > 5 ft. deep. Not for wastes containing ketones, nitrobenzene, dimethylformamide mesityloxide or tetrahydrofuran[1,2]
	b) Glass	Not for wastes containing hydrofluoric acid and concentrated alkali solution
Liquids and sludges in ponds, pits or lagoons	Pond	Cannot be used to collect samples beyond 12 ft. Dip and retrieve sampler slowly to avoid bending the tubular aluminum handle
Powdered or granular solids in bags, drums, barrels and similar containers	a) Grain sampler	Limited application for sampling moist and sticky solids and when the diameter of the solids is greater than ¼"
	b) Sample trier	May incur difficulty in retaining core sample of very dry granular materials during sampling
Dry wastes in shallow containers and surface soil	Trowel or scoop	Not applicable to sampling deeper than 3 inches. Difficult to obtain reproducible mass of samples.
Waste piles	Waste pile sampler	Not applicable to sampling solid wastes with dimensions greater than ½"the diameter of the sampling tube.
Soil deeper than 3 inches	a) Soil auger	Does not collect undisturbed core sample.
	b) Veihmeyer sampler	Difficult to use on stony or rocky or very wet soil.
Wastes in storage tanks	Weighted bottle sampler	May be difficult to use on very viscous liquids.

TABLE 2. CHOICE OF SAMPLE CONTAINER AND CLOSURE

Waste Types	Container and Closure
All types except pesticide, chlorinated hydrocarbons and hydrocarbons	Linear polyethylene bottles[a], wide mouth with plastic cap, 1000 ml and 2000 ml
All types except hydrofluoric acid, concentrated alkali	Glass bottles[b], wide mouth with bakelite cap and teflon film liner[c], 1000 ml and 2000 ml
Photosensitive wastes	Amber plastic or brown glass[d] bottle, 1000 ml and 2000 ml

---

[a] Nalgene, Cat. Nos. 2104-0032 and 2120-0005 or equivalent

[b] Scientific Products, Cat. Nos. 87519-32 and B7519-64 or equivalent

[c] Available from Scientific Specialties, P.O. Box 352, Randallstown, MD

[d] Scientific Products, Cat. Nos. B7528-050 and 7528-2L or equivalent

TABLE 3. SELECTION OF RESPIRATORY PROTECTIVE DEVICE

Hazard	Respirator
Oxygen deficiency	Self-contained breathing apparatus Hose mask with blower
Gaseous contaminant: Immediately dangerous to life	Self-contained breathing apparatus Hose mask with blower Gas mask
Not immediately dangerous to life	Air-line respirator Hose mask without blower Chemical-cartridge respirator
Particulate contaminant	Dust, mist, or fume respirator Air-line resporator Abrasive-blasting respirator
Combination of gaseous and particulate contaminants immediately danerous to life	Self-contained breathing apparatus Hose mask with blower Gas mask with special filter
Not immediately dangerous to life	Air-line respirator Hose mask without blower Chemical-cartridge respirator with special filter

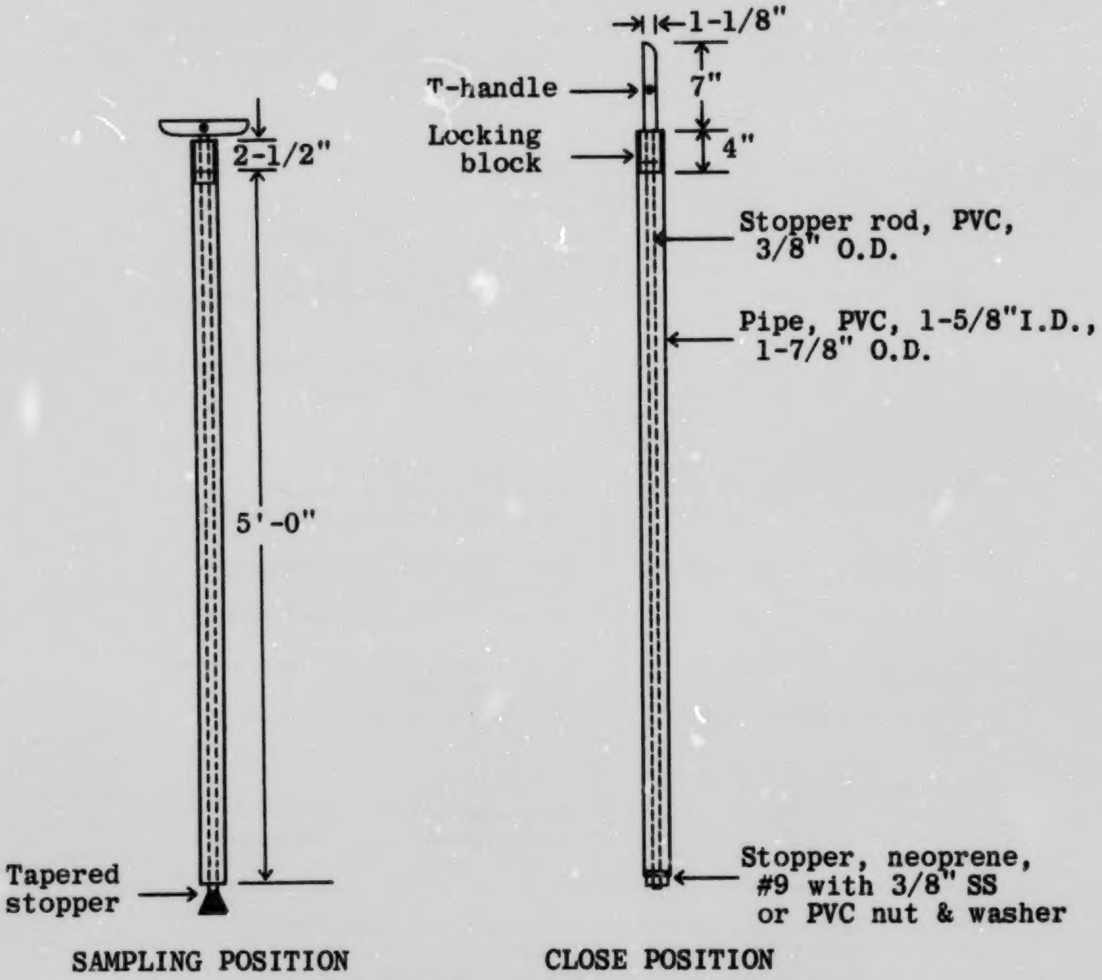
Source: "Respiratory Protective Equipment", Bulletin 226, Safety in Industry, Environmental and Chemical Hazards, No. 3, U. S. Dept. of Labor, Bureau of Labor Standards.

samplers are given in the Sampling Handbook.

COMPOSITE LIQUID WASTE SAMPLER (COLIWASA, FIGURE 2) DESCRIPTION

The Coliwasa is primarily applicable to sampling containerized liquid wastes such as those contained in vacuum trucks, barrels, drums, or similar containers. Its design permits the representative sampling of multiphase wastes of a wide range of viscosity, corrosivity, volatility and solid contents. It is simple and easy to use allowing rapid collection of samples thus minimizing the exposure of the sample collector to potential hazards from the waste during sampling. The sampler is not commercially available, but it is relatively easy and inexpensive to fabricate.

The first model of the Coliwasa was designed and fabricated in the California Department of Health.[3] This sampler was previously used in the collection of liquid waste samples in connection with the implementation of the hazardous wastes program of the Department. The sampler was also used in a case study jointly conducted for the U.S. Environmental Protection Agency by the University of Southern California and the Department.[4] This first model of the Coliwasa underwent a number of refinements and testing. The improved model of the Coliwasa is shown in Figure 2. The main



1-1/8"
T-handle
7"
Locking block
4"
2-1/2"
Stopper rod, PVC, 3/8" O.D.
Pipe, PVC, 1-5/8"I.D., 1-7/8" O.D.
5'-0"
Tapered stopper
Stopper, neoprene, #9 with 3/8" SS or PVC nut & washer
SAMPLING POSITION
CLOSE POSITION

FIGURE 2. COMPOSITE LIQUID WASTE SAMPLER (COLIWASA)

parts of the sampler consist of a positive quick-engaging closing and locking mechanism and a sampling tube.

Plastic and glass types of the Coliwasa have been constructed. The sampling tube and stopper rod of the plastic Coliwasa are made of translucent polyvinyl chloride (PVC) plastic while that of the glass Coliwasa are made of borosilicate glass and teflon plastic, respectively. The materials for constructing the two types of the Coliwasa are available at hardware stores and supply houses.

SAMPLING PROCEDURES

The two most common containers encountered in hazardous waste sampling are the 55 gallon drum and the vacuum truck. There are several other sampling situations encountered which will not be covered here, but are discussed in detail in a manual soon to be issued by EPA. Procedures for use of the Coliwasa have already been described. The prime problem confronting the field personnel is access to the hazardous waste.

Sampling a vacuum truck requires the person collecting the sample to climb onto the truck and walk along a narrow catwalk. In some trucks, it requires climbing access rungs to the tank hatch. These situations present accessability problem to the sample collector who in addition has to wear usually full protective sampling gear. Preferably, two persons should perform the sampling; one person to do the actual sampling and the other to hand the sampling device and stands ready with sample container and to aid in any problems. The sample collector positions himself to collect samples only after the truck driver has opened the tank hatch.

The Coliwasa was specifically designed to allow for access to drummed waste through a bung hole. However, sampling of drums requries extreme caution for they are frequently corroded and/or under pressure. In addition, many extremely hazardous materials are stored in drums. Opening the bung of a drum can produce a spark that might detonate an explosive gas mixture in the drum. This situation is difficult to predict and must be taken into consideration every time a drum is opened. The use of full protective sampling equipment can not be overemphasized when sampling a drum.

HAZARDOUS WASTE ANALYSIS

The analysis of hazardous wastes presents unique problems for the complexity of wastes is generally inversely proportional to their value and directly proportional to the cost of analysis. However, public health and environmental impacts are unrelated to value. Consequently any analytical scheme must be flexible and allow for general characterization of wastes as well as quantitative analysis. A four level analytical scheme has been proposed to provide this flexibility. The primary elements of the scheme are shown in Figure 3.

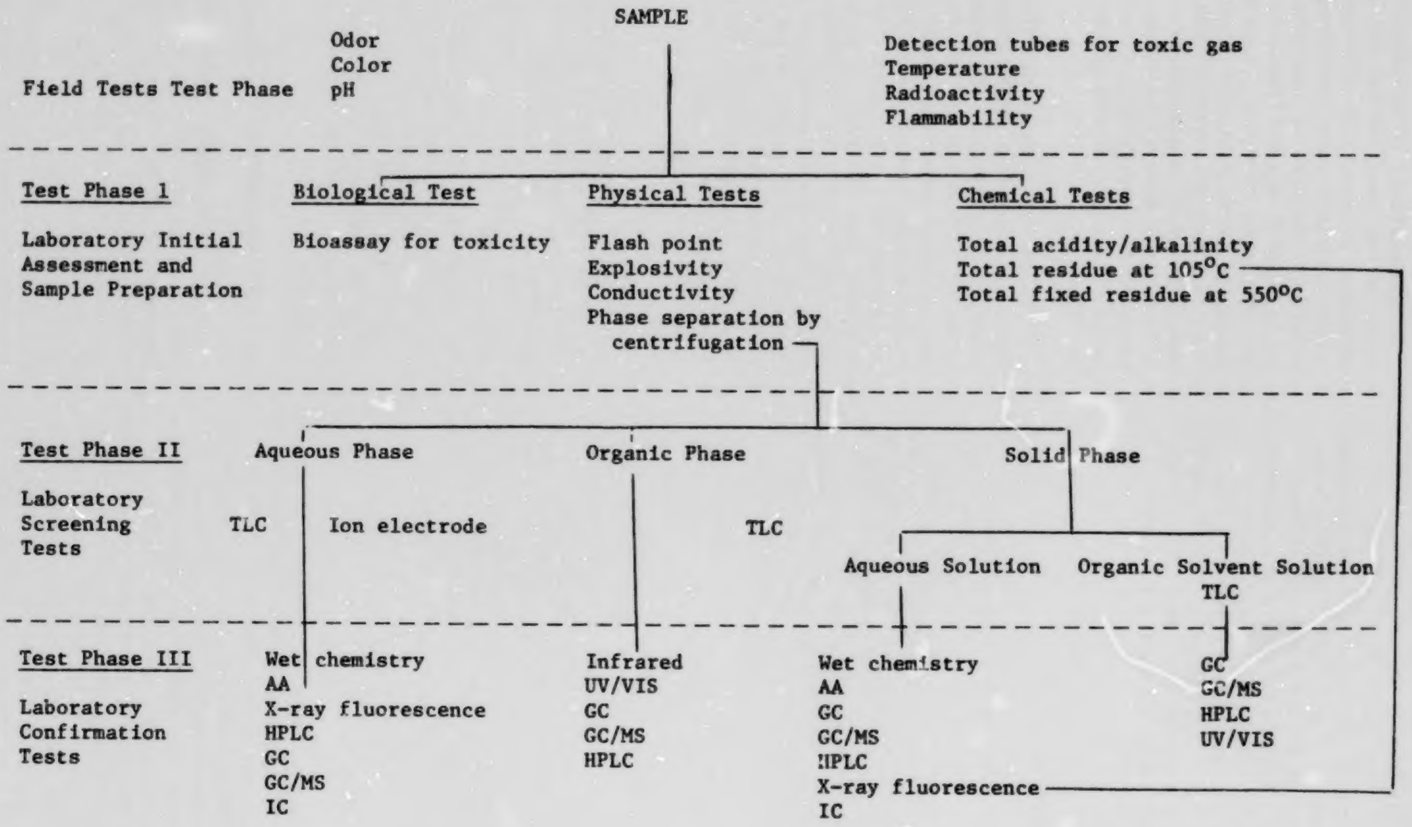
Field Tests Phase is intended for field assessment of waste physical and chemical properties. The primary objectives of this phase are two fold. They are to avoid immediate public health and environmental damage due to fire, explosion, or release of toxic gases. In addition, the tests are designed to give an approximate verification to composition information. Even though several of these tests are common, well characterized procedures, difficulties arise due to interferences from oily phases, solid phases, and excessive temperatures. Details of these procedures are discussed in the forthcoming handbook.

Phase I (Initial Laboratory Assessment and Sample Preparation). The objective of the initial laboratory phase is for confirmation of the field data and to provide more accurate physical property data possible under controlled laboratory conditions. This phase uses 105°C residue and 550°C residue tests to assess approximate levels of dissolved inorganic and organic components. The final step in this section involves high speed centrifugation (10-15K rpm) to separate the organic aqueous and solid phases.

PHASE II (LABORATORY SCREENING TEST)

The objective of this phase of the scheme is to provide for relatively rapid, inexpensive means for qualitative analysis of the separated phases. Emphasis is placed on noninstrumental methods where possible. A key element of this phase of the testing will involve the use of thin layer chromatography (TLC). This method is particularly valuable on wastes for which little background information is available. Procedures

FIGURE 3. ANALYSIS SCHEME FOR INDUSTRIAL WASTES


SAMPLE
Field Tests Test Phase
Odor
Color
pH
Detection tubes for toxic gas
Temperature
Radioactivity
Flammability
Test Phase 1
Laboratory Initial Assessment and Sample Preparation
Biological Test
Bioassay for toxicity
Physical Tests
Flash point
Explosivity
Conductivity
Phase separation by centrifugation
Chemical Tests
Total acidity/alkalinity
Total residue at 105°C
Total fixed residue at 550°C
Test Phase II
Laboratory Screening Tests
TLC
Aqueous Phase
Ion electrode
Organic Phase
TLC
Solid Phase
Aqueous Solution
Organic Solvent Solution
TLC
Test Phase III
Laboratory Confirmation Tests
Wet chemistry
AA
X-ray fluorescence
HPLC
GC
GC/MS
IC
Infrared
UV/VIS
GC
GC/MS
HPLC
Wet chemistry
AA
GC
GC/MS
HPLC
X-ray fluorescence
IC
GC
GC/MS
HPLC
UV/VIS

being proposed will involve selected banks of eluting solvent systems, stationary phases, and developing sprays which will identify organic functional groups and chemical classes as well as certain suspected and more commonly occuring standard compounds. Additionally, TLC, will provide for qualitative identification of a wide variety of inorganic compounds.

PHASE III (LABORATORY QUANTITATIVE ANALYSIS)

This phase of the scheme is a compilation of the state of the art instrumental methods for analysis of complex mixtures of organic and inorganic systems. Primary effort to date has been in the development of infrared, atomic absorption (AA) and x-ray fluorescence (XRF) spectroscopic methods. A new and powerful tool for the analysis of complex mixtures of metals, both solid and solution, is the polarized Zeeman AA spectrometer. The special feature of this instrument allows for automatic and effective correction for sample matrix effects and specific interferences. The use of the polarized Zeeman spectrometer has allowed for rapid analysis of waste samples directly, without sample preparation for a large number of metals. Another powerful tool for inorganic analysis is the XRF. XRF has proven particularly useful on wastes from unknown sources such as spills, soil samples, and illegal dumping. The method allows for simultaneous analysis of 40 elements with little or no sample preparation. New XRF methods currently under development will make possible direct 40 element analysis of any homogeneous aqueous or organic liquid. It is recognized that XRF requires specialized and expensive instrumentation. However, the rapidity with which complex samples can be analyzed does justify its use in areas where large amounts of industrial wastes are produced.

The next one to two years shall bring considerable development and refinement of the proposed analytical methods. Major effort will be placed toward the analysis of complex organic mixtures, particularly for those materials which because of their toxicity or persistence pose significant public health and environmental health hazards.

ACKNOWLEDGEMENT

The authors would like to fully acknowledge the valuable assistance of many coworkers at the California Department of Health as well as the financial assistance of the U.S. Environmental Protection Agency, Richard A. Carnes, Project Officer.

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CHARACTERIZING INPUT TO HAZARDOUS WASTE LANDFILLS

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ABSTRACT

The average concentration, estimated daily deposition, and partitioning of 17 metal species in hazardous waste landfills in the greater Los Angeles, California area were studied. These sites received a combined estimated 2.3 million liters per day of waste classified as hazardous requiring disposal at Class I sites. A total of 320 samples was collected and consolidated to 99 representing 17 industry types.

Mass deposition rates were determined by calculating the average concentration of the metal species in conjunction with approximate daily volume received at the site. Approximately 50 percent of the total volume of hazardous wastes sampled was generated by the petroleum industry. About 35 percent of the volume was equally divided between the chemical and industrial cleaning industries. Approximately 70 percent of the total volume was in the aqueous phase while 8 percent consisted of an organic liquid phase. Some recommendations concerning the interactions of hazardous wastes with differing soil types and the resulting effect on leachate formation and potential migration of the toxic metal species were proposed especially regarding the need for further research.

INTRODUCTION

In recent years, controls which further restrict emissions to air and discharges to water, as well as open dumping have increased the pressure to dispose of waste on land. Approximately 10 million tons of nonradioactive hazardous waste are generated annually with the total increasing by about 5 to 10% per year.(1) About 40% of these wastes by weight are inorganic, whereas 60% are organic; some 90% accurs as liquid or semi-liquid. Over 70% of all hazardous wastes are generated in the mid-Atlantic, Great Lakes, and Gulf Coast areas of the United States.(2) Although sanitary landfilling has been developed as a means of disposing of waste material in general, these sites were not specifically designed to handle hazardous wastes. Many hazardous wastes are, never the less, disposed of at conventional landfill sites. The problems associated with improper land disposal of these wastes, unlike those of air and water pollution, have not been widely recognized by the public. However, as bans on ocean dumping become more widespread, and pesticide cancellations increase the tonnages of hazardous wastes which must be removed from the environment, the concern for safe disposal also grows. The lack of reliable information has generated concern about the practice of confined land disposal of hazardous wastes. Few data are available on the concentrations of trace metals, chlorinated hydrocarbons, pesticides, and other toxic constituents of these wastes. The more comprehensive version of the study reported on here may be obtained by contacting the author.

EXPERIMENTAL

Liquid wastes were collected at five major Class I landfills in the Los Angeles basin: BKK in West Covina; Pacific Ocean Disposal (POD) in Wilmington; Operating Industries (OI) in Monterey Park; Calabasas (CB); and Palos Verdes (PV).

In any program of sampling hazardous wastes, the following parameters must be considered:

1. Phase complexity: Techniques must yield a representative sample, because hazard-

ous wastes appear in all phases: solid, aqueous, and organic liquid.

2. Access to waste: Hazardous wastes are usually contained in ponds, vacuum trucks, barrels, etc.; sampling procedures must be amenable to all of these.

3. Chemical Reactivity: Many wastes are either highly corrosive, strong oxidizers, or, because of their physical nature, very hard on sampling equipment. These features place severe demands on equipment design.

4. Safety: Because of the undefined nature of most hazardous wastes, extensive precautions must be taken by sampling personnel.

5. Sampling Containment and Preservation: The containment and preservation of corrosive, toxic, or volatile samples present many problems to sampling and analytical personnel.

SAMPLING HAZARDOUS WASTE

1. Sampling Teams: Each team consisted of three people. Two functioned primary as collectors and one as record keeper. Based on a review of manifests over a 1 year period, it was estimated that samples collected during the 2 week survey by two teams, represented 90% of the waste types received at the sites over a 1 year period. The remaining 10%, mainly seasonal types of disposal, could not be sampled during the course of this study.

2. Sampling Equipment Inventory: Table 1 lists the equipment requirements for each sampling team.

3. Sampling Procedures: The object of the program was to obtain representative samples of all liquid, sludge, and solid hazardous waste delivered to a disposal site. The following were stepwise procedures used for sampling incoming traffic:

   - Sampling personnel, intercepted waste truck, requested copy of manifest, recorded manifest number and appropriate information on waste sampling form (Appendix A), and requested driver to pull off main traffic flow and opened inspection hatch.

Table 1. Sampling Equipment

Equipment List
Sampling:
1. Three (3) sample tubes
2. Sample bottles
3. Funnels
4. Tube Cleaners
5. Disposable wipers
6. Drums, 1-55 gal.; 3-5 gal. pails
7. 5 gal.-1,1,1, Trichloro Ethane or Other Suitable Solvent
8. Spares: tubes
9. Spares: rods
10. Spares: stoppers
11. Ink pens: Mark-on-anything
12. Tool Kit
13. Clip Board
14. Analytical forms
15. First Aid Kit
Personnel: each team
3 protective suits
2 hard hats with shields
boots for each sampler/not necessary for record keeper
2 respirators
4 pair gloves
2 pair goggles

   - Sampling personnel, properly attired with safety equipment, climbed onto truck and lowered the specially designed composite liquid waste sampler (Coliwasa) (Figure 1) into the liquid to obtain a representative cross section of hazardous waste. The waste samples were then transferred directly to a one-liter polyethylene container.

   - Containers were appropriately numbered and stored on the sampling truck approximately 4 days before transfer to 4°C storage.

A schematic of the sample collection, preparation, and analysis, is presented in Figure 2.

Analytical Methods

1. General Parameters: Solids content (total, soluble and insoluble), pH, acidity, and alkalinity were measured in accordance with procedures described in Standard Methods, 14th Edition.(3) Mineral acidity and total alkalinity were determined by

potentiometric titration to pH 4. Flash point was measured using ASTM Standard Method, D1310-72.(4) Phase distribution (organic, aqueous, solid) was determined by centrifugation for 10 minutes at 12,000 RPM; the separated phases were removed and recorded as a weight percent. Volatile organics were identified by distillation of the organic phase at 95°C with a Kontes microsteam distillation unit.

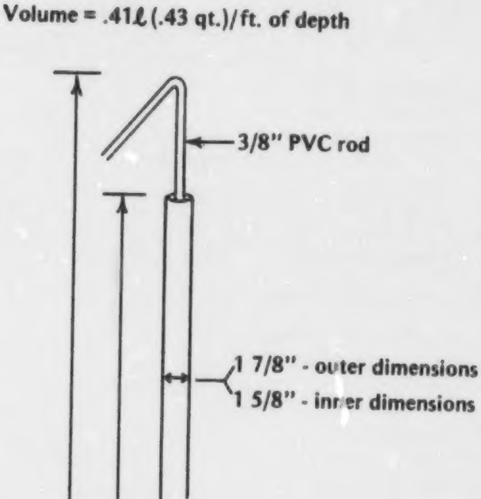
Volume = .41ℓ (.43 qt.)/ft. of depth
3/8" PVC rod
1 7/8" - outer dimensions
1 5/8" - inner dimensions
Class 200 PVC pipe
72"
60"
No. 9½ neoprene stopper
3/8" S.S. nut and washer

FIGURE 1. COMPOSITE LIQUID WASTE SAMPLER (CoLiWaSa)

2. Metal Species: Sample preparation is presented in Appendix B. Seventeen metal species were analyzed; Be, Na, Ag, Mg, K, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, Ba, and Pb. All analyses were performed on a double beam atomic absorption spectrophotometer equipped with a HGA 2100 graphite furnace. Na and K were analyzed using emission flame photometry. The graphite furnace was employed in the analysis of As and Cd, toxic elements in low concentration, and Be, V, and Ba which require special fuel when analyzed by flame methods. More details on the analytical portion of the project are presented in the comprehensive report mentioned above.

RESULTS AND DISCUSSION

A total of 320 waste samples were collected, and duplicates (those originating from the same source were identified and sorted so that one representative of each duplicate set would be analyzed.

The calculated mass deposition rates are based on the total volume inputs estimated by the Class I site operators. The data indicate that the highest average daily mass deposition of metal species is generated by the following industries:

Petroleum	As, Be, Ca, Cd, K, Mg
Chemical	As, Na
Industry Cleaning	Pb
Metal	Cr, Zn
Misc./Unknown	Ba, Cu, Fe, Mn, Ni

The volume flow and concentration of soluble toxic metals present a potential threat to the quality of ground and surface water supplies. Physical and chemical properties of the soil which may be affected include attenuation and field capacity, flocculation or dispersion of clay particles, hydraulic conductivity, infiltration rates; toxic elements may also accumulate.

Leachate will not be produced until a sizeable portion of the landfill has reached field capacity. However, some leachate may be produced immediately after initially wet waste is compacted and disposed of or liquid

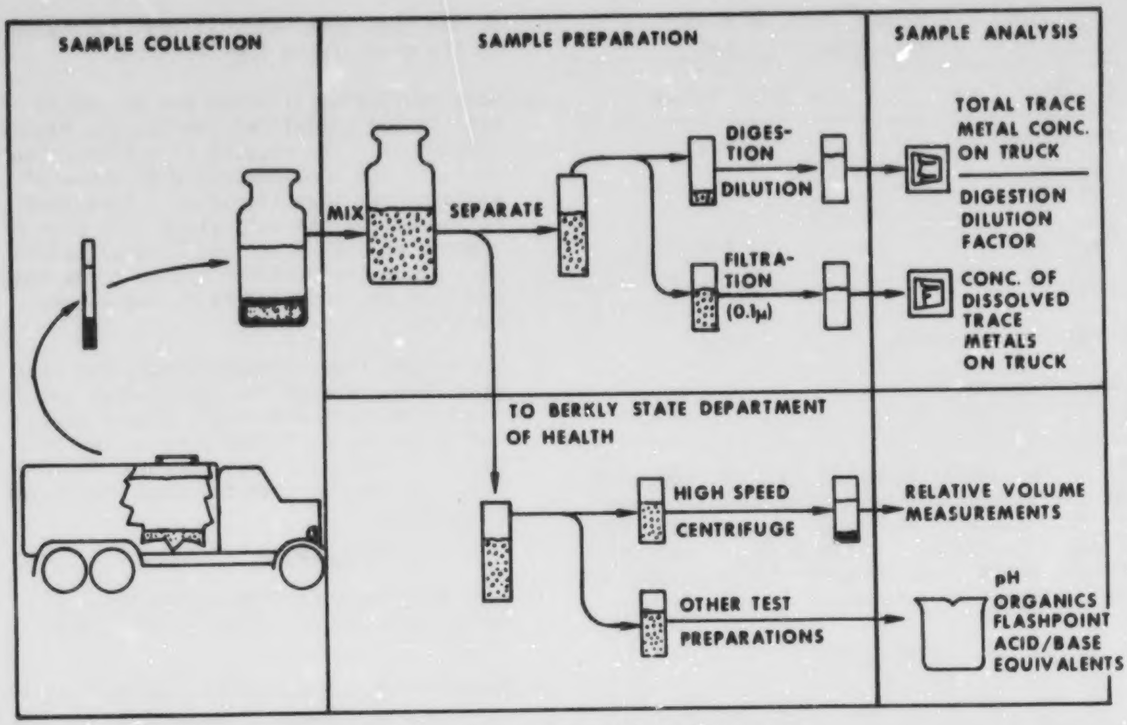
SAMPLE COLLECTION
SAMPLE PREPARATION
SAMPLE ANALYSIS
MIX
SEPARATE
DIGESTION
DILUTION
FILTRATION
(0.1μ)
TOTAL TRACE METAL CONC. ON TRUCK
DIGESTION DILUTION FACTOR
CONC. OF DISSOLVED TRACE METALS ON TRUCK
TO BERKLY STATE DEPARTMENT OF HEALTH
HIGH SPEED
CENTRIFUGE
RELATIVE VOLUME MEASUREMENTS
OTHER TEST
PREPARATIONS
pH
ORGANICS
FLASHPOINT
ACID/BASE EQUIVALENTS

FIGURE 2. SCHEMATIC OF SAMPLE HANDLING

is channeled through the fills. If concentrations of hazardous wastes are high in the leachate, the soil attenuation capacity may be reached relatively quickly. The cation exchange capacity will vary with the nature and concentration of ions in solution. Clay particles may either flocculate or disperse depending on their state of hydration and the composition of their exchangeable cations. Dispersion usually occurs with monovalent and highly hydrated cations, for example, Na. Conversely, flocculation occurs at high solute concentrations and/or in the presence of divalent and trivalent cations.(5) Because of various chemical, physical, and biological processes, hydraulic conductivity may change as liquid permeates the soil and flows through it. The composition of the exchangeable-ion complex when, for instance, leachate enters soil changes because the concentration of solutes differs from that of solution; this can greatly alter hydraulic conductivity.(6-8) Further studies on the interactions of hazardous wastes and soil, particularly on the effect upon hydraulic ocnductivity and particle size distribution are called for.

From the analysis, we can project the estimated daily deposition rate according to species as follows:

Total: Na>Fe>Ca>Zn>K>Mg>Cu>Cr>Ni>Pb>Ba>Mn>V>Cd>As>Be>Ag

Soluble: Na>Fe>Ca>Cu>Zn>K>Cr>Mg>Ni>Pb>Mn>Ba>V>Cd>As>Ag>Be

Solid: Na>Ca>Fe>Mg>Zn>K>Pb>Cu>Cr>Ba>Ni>Mn>V>Cd>As>Be>Ag

Approximately one-half of the total volume of hazardous wastes was generated by the petroleum industry. About 35% was contributed by the chemical and industrial cleaning industries. The total volume contribution is shown in Table 2.

About 70% of the estimated total volume input of 2.3 X 16^6 ℓ/day is in the aqueous phase and 8% consists of an organic liquid phase, 16% of which is volatile (B. Pt. less than 95°C).

Table 2. Volume Input Generated by General Industry Types

Industry Type	% Total Volume
Petroleum	45.9
Chemical	17.9
Metal	6.0
Food	3.6
Industrial Cleaning	17.4
Misc./Unknown	9.2

The results reported on here represent an overview of the more comprehensive report, "A Case Study of Hazardous Wastes Input Into Class I Landfills." This work was sponsored by the USEPA under Research Grant R803813 to the University of Southern California.

CONCLUSIONS

The following conclusions are based on results of sampling and analysis of hazardous wastes received at the five Class I landfills.

1. Average concentrations, estimated average daily inputs, and the partitioning of metal species (soluble and solid phase) varied widely for the five sites.

2. The data collected for individual sites, together with the estimated daily volume input, provide the approximation of mass deposition rates for selected metal species at a specific site.

3. Results show that wastes containing copper, chromium and zinc pose the greatest threat to possible groundwater and surface water contamination when the following factors are considered: (a) total mass deposition, (b) weight percent in the soluble phase, and (c) maximum concentration levels of 14,000-20,000 mg/l.

4. About 8% of total volume input was comprised of organic liquid wastes and 16% of the organic phase had boiling points of less than 95°C and flash points as low as 17°C.

5. The combined results for the five Class I sites is considered a first approximation of the hazardous waste streams generated in the greater Los Angeles area.

6. Some manifests collected and evaluated against the analytical results are highly suspicious. The results of certain metal analysis are incompatible with those of waste stream identification. Continued refinement of the data along with adequate support at both State and Federal levels will prove the manifest system to be quite workable and informative to regulatory agencies.

7. The volume flow, concentration, and mass deposition rate of the toxic metal species identified from this study should prove useful in the preliminary selection of required treatment processes and facilities for hazardous wastes from industrial activities.

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6. Brooks, R.H. et al., "The Effect of Various Exchangeable Cations upon the Physical Condition of Soils," Soil Science Soc. Amer. Proc., 20, 1956, pp. 325-327

7. Quirk, J.P. and R.K. Schofield, "The Effect of Electrolytic Concentration on Soil Permeability," J. Soil Science, 6, 1955, pp.163-170

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APPENDIX A

HAZARDOUS WASTE UNIT

SURVEILLANCE FORM

Sample OI 122 Lab No. ______ Sampling Date 9/12/75

Manifest No. 1411 Time 11:35

Producer Beth. Stl. Corp.

Producer's Address 3300 E. Slauson Ave., Vernon

Hauler Capri Pumping Service

Hauler's Address 3128 Whittier Blvd., Los Angeles, CA

Process Type Steelmaking Waste Type Mud and Water

Chemical Components	Concentration upper	Concentration lower	Volume	(units)
EE-203	85%	60%		
AL 203	5%	2%		
Grease	5%	2%		
SIO-2	2%	1%		

Brief Physical Description Black Liquid

APPENDIX B

SAMPLE PREPARATION

Preparation for filtration and digestion included thorough washing of all labware which would come in contact with samples. The following washing procedure was used: Scrubbing with a brush using detergent and industrial water. Rinsing three times with deionized water. Drying in low temperature oven. Storing in washed polyethylene bags.

Samples were stored at 4°C within the original one-liter plastic containers. After one week, about one-third of each sample was poured into identical, labeled containers and sent to the State Department of Health for analysis of organics and determination of percent liquid and solid volumes. Samples were returned to 4°C storage until aliquots were taken for filtration and digestion. Samples were kept at room temperature for approximately two days during this process. One aliquot was poured first through a #1 Whatman Filter and then passed through a 0.1 nm millipore filter into a sample bottle. Another aliquot (5 ml) was placed in a teflon beaker and digested with HNO_3, HF and $HClO_4$. The resulting liquid was centrifuged, poured into sample bottles, and diluted.

Sample Analysis

The partitioning of trace metals between those in the soluble phase and those associated with nonfilterable solids was attained by analyzing the filtrates (0.1 nm) and the acid digested total sample. Nonfilterable solids are then determined by subtracting dissolved trace metal concentrations from total concentrations.

"CO-DISPOSAL OF INDUSTRIAL AND MUNICIPAL WASTE IN A LANDFILL"

By:

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ABSTRACT

A research effort was initiated in late 1974 to study the effects of the co-disposal of selected industrial wastes with municipal refuse in a sanitary landfill environment. Observations were made utilizing 1.5 tonne test cells designed to closely simulate sanitary landfill field conditions. Six types of industrial wastes were mixed with municipal solid waste during loading. The six types of industrial wastes were petroleum sludge, battery production waste, electroplating waste, inorganic pigment waste, chlorine production brine sludge, and a solvent based paint sludge. All test cells received infiltration water additions equivalent to 406 mm (16 inches) per annum. Leachate samples were collected and analyzed on a monthly basis. The results of these analyses over a two and one half year period were compared with control cells containing only municipal refuse. The observations made resulted in the identification of a number of potential problem areas and recommendations for future research in this area.

Concurrent to this leachate study, the composition of gases generated in simulated landfill environment were investigated. The results of the gas composition study were noteworthy in that they indicated that methane production in landfilled refuse varied in a cyclic manner rather than the straight forward theoretical manner which was indicated in earlier studies. This apparent cyclic production of methane was possibly caused by a cyclic dominance of different types of microbial colonies in the landfill. The state of flux of the microbial colonies varies on a cycle which is dependent on several possible environmental factors.

INTRODUCTION

Solid Waste disposal has been a problem for society since its earliest beginnings. Until recently the "out of sight, out of mind" syndrome has been in effect. That is, no one apparently cared what happened to their waste once the refuse hauler took it. With a recent awakening of environmental awareness, brought about by a realization that our resources and land areas are not infinite, the population in general is more concerned with the final disposal of their waste.

In a non-industrial society the magnitude of the solid waste disposal problem was formerly a function of the size of the population. While this is still true to a degree, the recent trend in legislation as well as new innovations and refinements of waste treatment processes are bringing to the fore sewage sludge disposal problems which were heretofore largely ignored. Add to this the problem of ultimate disposal of the vast amount of industrial sludges, many of which are of a protentially hazardous nature, which are by-products of modern technological advancement and the situation has taken on an entirely new dimension.

While there are many new treatment processes either in use or undergoing testing today, the oldest form of solid waste disposal, namely landfilling, is still the most widely used method employed for the ultimate disposal of wastes.

Congress recognized the need for solutions to the problems of modern solid waste disposal and through various legislation, especially the Resource Conservation and Recovery Act of 1976, has mandated that research be accomplished to provide the information needed to properly design new landfills and to determine the environmental controls necessary to protect man from himself.

The disposal of refuse through the utilization of landfilling techniques presents a number of potential problem areas which need to be resolved. These are as follows:

1. The mechanics of simply handling the vast amounts of solid refuse generated by a modern society.

2. The geographical location of new landfill sites.

3. The needs of the design engineer for useful data with which to plant environmentally acceptable landfill sites.

4. The infiltration of ground water resources through the leaching processes.

5. The pollution of nearby surface waters via runoff.

6. The generation of potentially flammable and explosive gaseous mixtures in a decomposing landfill.

7. The landfilling of new, potentially hazardous, industrial wastes.

The disposal of refuse in a landfill leads to a number of problem areas related to the design and operation of the landfill site. The major problems historically associated with landfills have always been primarily operational in nature. However, society's modern day capacity for generating solid waste has made it necessary to consider other problem areas which heretofore were given little attention. These problem areas were discussed in the preceeding paragraphs. In June 1974, SYSTECH was contracted by the Solid and Hazardous Waste Research Division of the USEPA to investigate some of the problem areas which must be understood in order to properly maintain and control the situation which is occurring within the landfill itself.

This paper concerns itself with one phase of that overall study and embraces the problem of co-disposing industrial wastes of various types with municipal solid waste. For the purposes of this study sewage sludge is considered in this category. In addition the following types of bona fide industrial sludges were considered.

1. Petroleum Sludge

2. Battery Production Waste

3. Electroplating Waste

4. Inorganic Pigment Waste

5. Chlorine Production Brine Sludge

6. Solvent Based Paint Sludge

Due to the variety and number of co-disposal systems involved in this study replication of the test cells was not possible. Therefore, it must be noted that this is an observation study and the recommendations at this point must be limited to suggestions of possible problem areas and situations in which further indepth work is needed.

FACILITY DESCRIPTION

The experimental landfill test cells employed for this study are located at the USEPA Center Hill Research Facility in Cincinnati, Ohio. The total facility consists of fifteen outside cells buried in the ground, along with a leachate collection well and an instrumentation building. An additional four test cells are located in the northeast corner of enclosed high bay area directly adjacent to the research facility. Of these nineteen cells, nine were loaded with either co-disposed industrial waste or co-disposed municipal sewage sludge. It is these nine cells plus control cells loaded with municipal solid waste only which are the primary considerations of this paper.

The test cells proper are 1.8m (6 ft.) in diameter and 3.6m (12 ft.) deep. They are constructed of 4.76mm (3/16 in.) steel covered with coal tar epoxy. The outside test cells were placed on top of concrete bases and the excavated area backfilled with soil to approximately 0.3m (1 ft.) from the top of the test cells. Several layers of fiberglass cloth were placed at the base of the cells and extended up the interior walls to a height of approximately 0.3m (1 ft.) and epoxied in place in an attempt to insure quantitative leachate and gas collection. The four interior cells have steel bases welded onto the main tube of the cell.

Provisions for draining leachate have been included in the construction of the bases of all the cells. The outside test cells have a depression in the concrete base of the test cell with piping to the central leachate collection well. The cells located in the enclosed bay area are mounted on concrete pedestals allowing the center section of the base of the cells to be exposed for leachate collection.

Water additions are made to the cells by means of a distribution system composed of perforated tube formed into a circle. The circular tubing is connected through the wall of the test cells to a hose connection where water is introduced in accordance with a predetermined rainfall application schedule. The interior distribution tube is located within the pea gravel layer to aid in uniformly distributing the water addition over the surface of the clay cover.

Figure 1 shows a cross section of a completed test cell. At the base of the cell is a 150mm (6 in.) layer of silica gravel. Above the silica gravel were eight lifts of solid waste, each 0.3m (1 ft.) in thickness. Temperature probes are located at the second, fourth, and sixth lifts, while gas probes are located at the second and sixth lifts and in the pea gravel cover.

The observation well for leachate collection is a well 4.8m (16 ft.) deep and 1.8m (6 ft.) in diameter with a scaling ladder welded to the interior wall of the cell for access purposes. All of the leachate drains from the exterior cell are connected to this observation well and valved at this central collection point.

TEST CELL CONTENTS

The purpose of the study is to observe the potential effects of the co-disposal of industrial wastes with municipal solid wastes on the landfill environment. The municipal solid waste used in the study was obtained from the City of Cincinnati, Ohio. A brief description of each of the industrial waste types mixed with the MSW is given in the following discussion (Table 1).

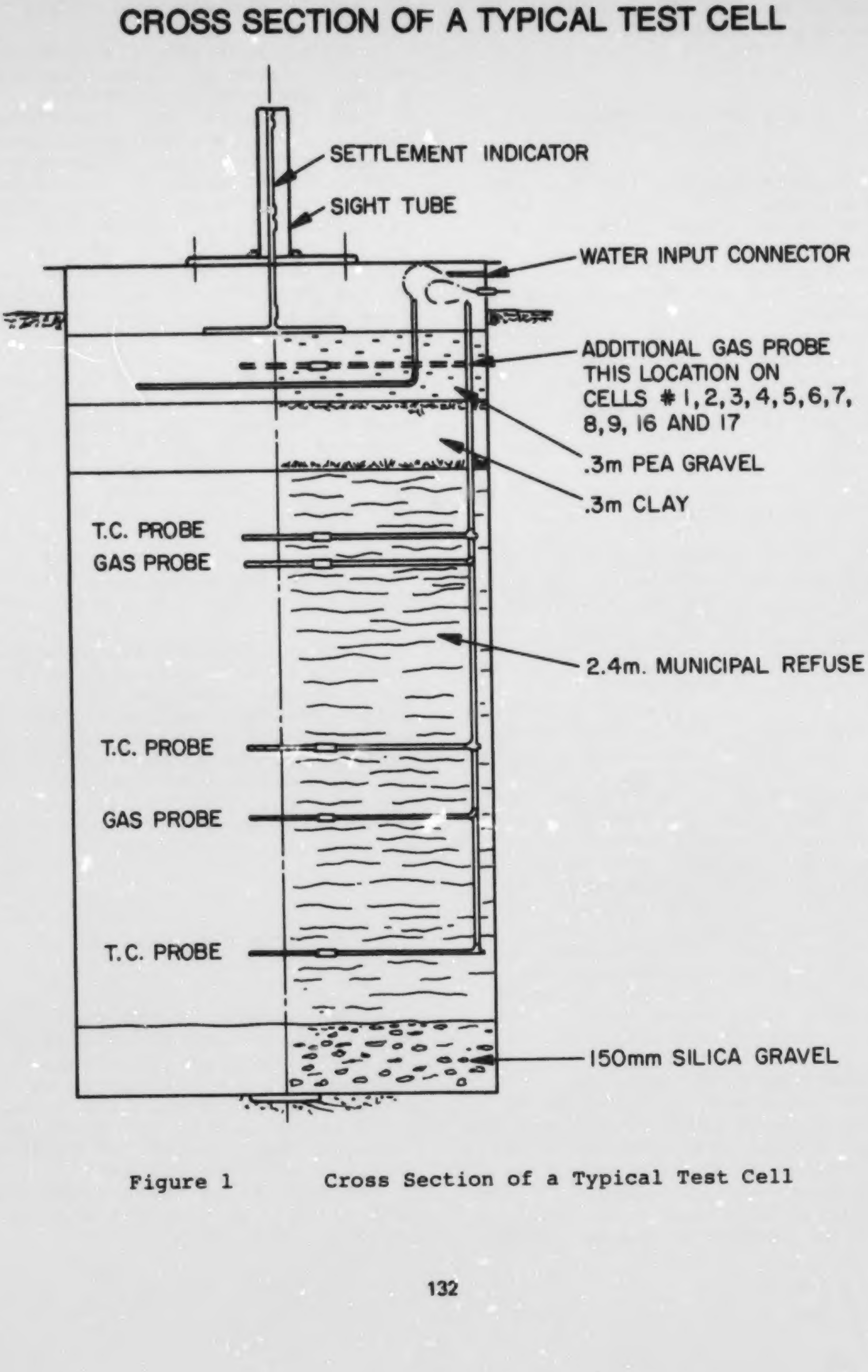
CROSS SECTION OF A TYPICAL TEST CELL
SETTLEMENT INDICATOR
SIGHT TUBE
WATER INPUT CONNECTOR
ADDITIONAL GAS PROBE THIS LOCATION ON CELLS # 1, 2, 3, 4, 5, 6, 7, 8, 9, 16 AND 17
.3m PEA GRAVEL
.3m CLAY
T.C. PROBE
GAS PROBE
2.4m. MUNICIPAL REFUSE
T.C. PROBE
GAS PROBE
T.C. PROBE
150mm SILICA GRAVEL

Figure 1   Cross Section of a Typical Test Cell

Table 1 Summary of Additive Materials Placed in Test Cells

TEST CELL	ADDITIVE	AMOUNT ADDED PER LIFT (kg, WET WEIGHT)								MOISTURE CONTENT	WEIGHT (kg)	
		1	2	3	4	5	6	7	8	PERCENT BY WET WEIGHT	WET WEIGHT	DRY WEIGHT
5	SEWAGE SLUDGE	0	9.7	9.7	9.7	9.7	9.7	9.7	9.7	88	68	8.20
6	SEWAGE SLUDGE	0	29.2	29.2	29.2	29.2	29.2	29.2	29.2	88	204	24.5
7	SEWAGE SLUDGE	0	97.2	97.2	97.2	97.2	97.2	97.2	97.2	88	680	81.6
9	REFINERY SLUDGE	0	216.9	216.9	216.9	216.9	216.9	216.9	216.9	79.0	1518	319
10	BATTERY PRODUCTION WASTE	0	184.4	184.4	184.4	184.4	184.4	184.4	184.4	89.2	1291	152
12	ELECTROPLATING WASTE	0	170.1	170.1	170.1	170.1	170.1	170.1	170.1	79.5	1191	244
13	INORGANIC PIGMENT WASTE	0	202.9	202.9	202.9	202.9	202.9	202.9	202.9	51.7	1420	686
14	CHLORINE PRODUCTION SLUDGE	0	291.3	291.3	291.3	291.3	291.3	291.3	291.3	24.1	2039	1550
17	SOLVENT BASED PAINT SLUDGE	0	229.2	229.2	229.2	229.2	229.2	229.2	229.2	24.7	1604	1210

In the primary treatment of oily wastes the wastewater is sent to a API separating tank, then to an air flotation unit. All the oily sludges are then sent to a holding tank where chemicals are added to removed most of the oil. The sludge used in this project consists of the bottoms from the holding tank, and contains slightly more emulsified oil than API bottoms sludge.

The battery production waste was obtained from a manufacturer of lead/acid storage batteries. This waste is a composite from all phases of a manufacturing operation with the exclusion of the battery plate assembly section itself. The composite processing wastes were neutralized and discharged to a settling pond. The sludge used in this program was obtained from this settling pond.

The electroplating waste was obtained from a large plating firm which employs the following plating processes: chromium (Cr), nickel (Ni), cadmium (Cd), copper (Cu), iron (Fe), and zinc (Zn). After employing various treatment processes to neutralize and breakdown the wastes the treated wastes are pumped to a lagoon for settling. The settled sludge used in this program was a brown soupy material with high moisture content.

The inorganic pigment waste was obtained from a supplier whose main product was titanium dioxide. The wastewaters from the various manufacturing operations in this plant are treated simultaneously. The resulting settled sludge was dewatered. The waste used in our program was this dewatered sludge.

The chlorine production brine sludge was obtained from a manufacturer which employed the mercury cell technique for chlorine liberation. The major portion of the sludge used in the landfill program (60 to 80 percent) was from the brine saturator while the remainder was from the clarifier after settling. The sludge used appeared somewhat moist, brown in color, and very dense.

The solvent-based paint sludge used was representative of a paint sludge produced in industries where a water curtain is used to capture overspray. The water was pumped directly to a holding tank for disposal with no pretreatment. The material contained organic solvents and was extremely viscous, its color dependent upon the pigments present.

Some notable components of these sludges were: copper (Cu), iron (Fe), mercury (Hg) in the refinery sludge; copper (Cu), iron (Fe), cadmium (Cd), lead (Pb), asbestos, tin (Sn), antimony (Sb) in the battery production waste; chromium (Cr), iron (Fe), arsenic (As), cadmium (Cd), cyanide, asbestos in the inorganic pigment waste; and nickel (Ni), lead (Pb), chloride, asbestos, mercury (Hg) in the chlorine production brine sludge.

MOISTURE DATA

The field capacity of refuse is its absorptive capacity for moisture. Theoretically, once field capacity is reached in a landfill environment, the amount of water infiltrating the landfill should equal the quantity of leachate existing the landfill.

Utilizing a definition as given by Fenn et al[1], "field capacity" is the maximum moisture which a soil (or solid waste) can retain in a gravitational field without producing continuous downward percolation. In the case of this study the appearance of collectible leachate volumes on a continuous basis was indicative that field capacity had been reached according to the definition above.

In order to evaluate potential effects of the co-disposal of industrial wastes in a municipal landfill, moisture additions were made to the simulators and were varied monthly as one would expect the rainfall pattern to be in the midwestern U.S. The total moisture added to each cell was equivalent to the infiltration of 406mm (16 in.) of water per annum.

The moisture retention capacity of the test cells was determined by the water balance method. This method considers the initial moisture content of the refuse, the moisture content of the industrial wastes added, the volume of water added to the cell as part of the moisture addition regiment, and the quantity of leachate removed from the test cell with time. Utilizing the above parameters the water retained in the cell was described as follows:

$$\text{water retained (ml/kg)} = \frac{\text{initial moisture content + water added - leachate removed}}{\text{kg solid waste (dry wgt.)}}$$

The test cells containing the various co-disposed industrial wastes exhibited a high initial moisture content. A significant part of this initial moisture content was contributed by the industrial waste additive. For example, the moisture content of the petroleum sludge was approximately 80 percent by wet weight; the battery waste was approximately 90 percent moisture; the electroplating waste was approximately 80 percent moisture; the inorganic pigment waste was approximately 51 percent moisture. These industrial waste sludges are typical in that they have a high moisture content and would be representative of sludges obtained by a by-product of a waste treatment operation which did not employ mechanical dewatering techniques. The resulting effects of adding the high moisture content sludges to landfilled municipal refuse would appear to be a more rapid attainment of apparent field capacity (with the attendant onset of leaching) than is the case with municipal waste only. (Table 2) This was true in all cases except for the solvent based paint sludge cell which began continuous leaching at approximately the same time at the MSW only cell. This again was more or less expected as the paint sludge contained about 25 percent moisture while the other additives contained from two to four times as much initial moisture.

Table 2 Water Balance Summary

Test Cell	Time To Reach F.C.* In Months	Water Added		Average Moisture Retained In Cell Subsequent To Reaching F. C. (l)	Average Moisture Retained (ml/kg Solid Waste)
		mm	l		
2	16	516	1357	$\bar{x}$ 2899 σ ±80 (2.7%)	$\bar{x}$ 1688 σ ±46 (2.7%)
5	16	516	1357	$\bar{x}$ 2565 σ ±81 (3.2%)	$\bar{x}$ 1449 σ ±46 (3.2%)
6	16	516	1357	$\bar{x}$ 2764 (3.1%) σ ±87	$\bar{x}$ 1745 (3.2%) σ ±55
7	16	516	1357	$\bar{x}$ 2596 (3.4%) σ ±89	$\bar{x}$ 1784 (3.4%) σ ±61
9	13	368	969	$\bar{x}$ 3567 (2.2%) σ ±78	$\bar{x}$ 1480 (2.2%) σ ±32
10	1	74	194	$\bar{x}$ 2554 (2.9%) σ ±75	$\bar{x}$ 1407 (2.9%) σ ±41
12	5	184	485	$\bar{x}$ 2855 (5.2%) σ ±150	$\bar{x}$ 1200 (5.3%) σ ±63
13	7	331	872	$\bar{x}$ 2628 (5.7%) σ ±151	$\bar{x}$ 1029 (5.7%) σ ±59
14	5	184	485	$\bar{x}$ 2402 (4.5%) σ ±107	$\bar{x}$ 663 (4.5%) σ ±30
17	16	516	1357	$\bar{x}$ 2930 (3.9%) σ ±115	$\bar{x}$ 892 (3.9%) σ ±35
18	11	331	872	$\bar{x}$ 2364 (7.2%) σ ±170	$\bar{x}$ 1146 (7.2%) σ ±82
19	13	368	969	$\bar{x}$ 2452 (3.2%) σ ±78	$\bar{x}$ 1178 (3.2%) σ ±38

* Field capacity is defined as the maximum moisture content which a soil (or solid waste) can retain in a gravitational field without producing continuous downward percolation. (Ref. 1) Data is presented in terms of "field capacity" meaning the initiation of continuous leachate production.

LEACHATE DATA

In order to evaluate the possible effects on leachate characteristics by the co-disposal of different industrial wastes with municipal refuse, the following industrial wastes were added during the loading sequence for the following cells:

Cells 5,6,7	Sewage Sludge
Cell 9	Petroleum Sludge
Cell 10	Battery Production Waste
Cell 12	Electroplating Waste
Cell 13	Inorganic Pigment Waste
Cell 14	Chlorine Production Brine Sludge
Cell 17	Solvent Based Paint Sludge

Cells 5, 6, 7, 12, 13, 14, and 17 were loaded in November 1974. The leachate data from these cells are compared with that from cell 2 and cell 16 containing only municipal refuse which were also loaded in November 1974. (Figure 2-14) Cells 9 and 10 were loaded in April 1975 and are compared to cells 18 and 19, containing municipal refuse only, which were also loaded in April 1975. (Figures 15-19)

The data collected from the landfill simulators containing sewage sludge in addition to the municipal refuse seem to indicate that such disposal will not present a major problem. This conclusion is based on the fact that when comparing the cumulative amounts of the various pollutants produced from each cell, no generalized effect due to the addition of varying amounts of sewage sludge was noted. There were some individual parametric differences, however, examination of the data traced these differences primarily to some channeling effects which occurred in cell 5 early in the study.

The data garnered to date from the cell containing the co-disposed petroleum sludge indicates some rather interesting phenomena. petroleum sludge appears to inhibit the leaching process. This is possibly due to a coating action whereby the decomposition of the waste and the solubilization of components of the waste is inhibited. While it is recognized that this data was gathered from a single cell, without replication, it is felt that this phenomenon should be the subject for a future in-depth study to investigate the possibility of the coating breaking down with the subsequent production of a highly polluted leachate stream.

Observations made of the data generated by the cell containing co-disposed battery production waste indicate that in most cases the leachate pollutant concentration was greater than that found in the control cell containing municipal refuse only. This is an indication of potential problems in the landfilling of such wastes and more in-depth studies should be undertaken before landfilling practices are approved.

Data gathered from the cell containing co-disposed electroplating waste indicate that there is again an apparent enhancement effect on leachate strength which is shown by the increase in concentration of those leachate parameters which are indicative of the presence of electroplating wastes. These parameters are COD, total and dissolved solids, chlorides, copper, chromium, and nickel. The possible effects of the co-disposal of this waste on the surrounding ground water must be seriously evaluated prior to disposing of these wastes in a municipal landfill.

The test cell containing municipal refuse co-disposed with inorganic pigment waste provided data which, during the time period covered by this paper, exhibited no great differences between this cell and the municipal refuse only cell which was used as a control.

Chlorine brine sludge, on the other hand, when co-disposed over

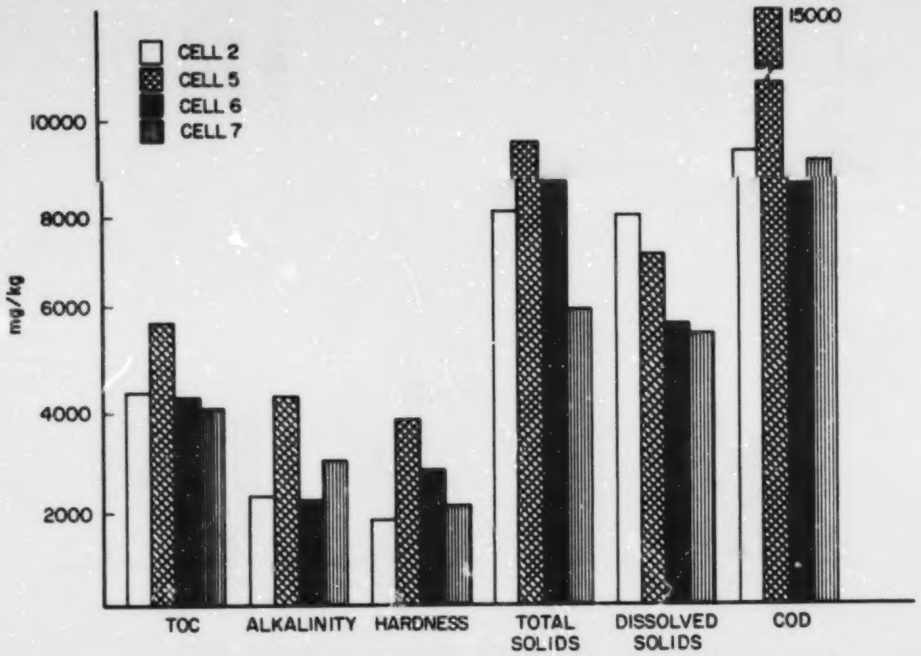

Figure 2 MSW/Sewage Sludge Data

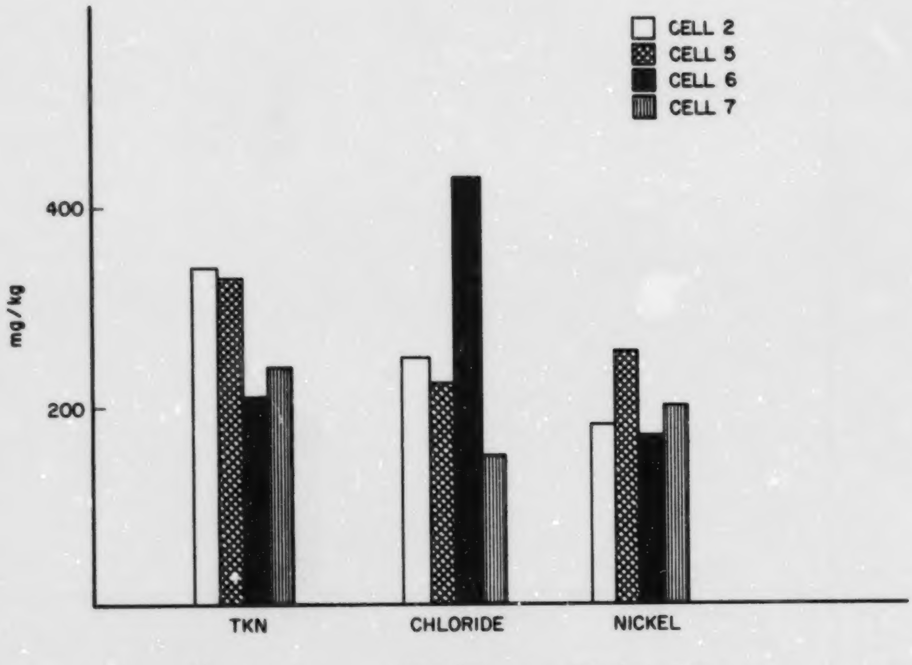

Figure 3 MSW/Sewage Sludge Data

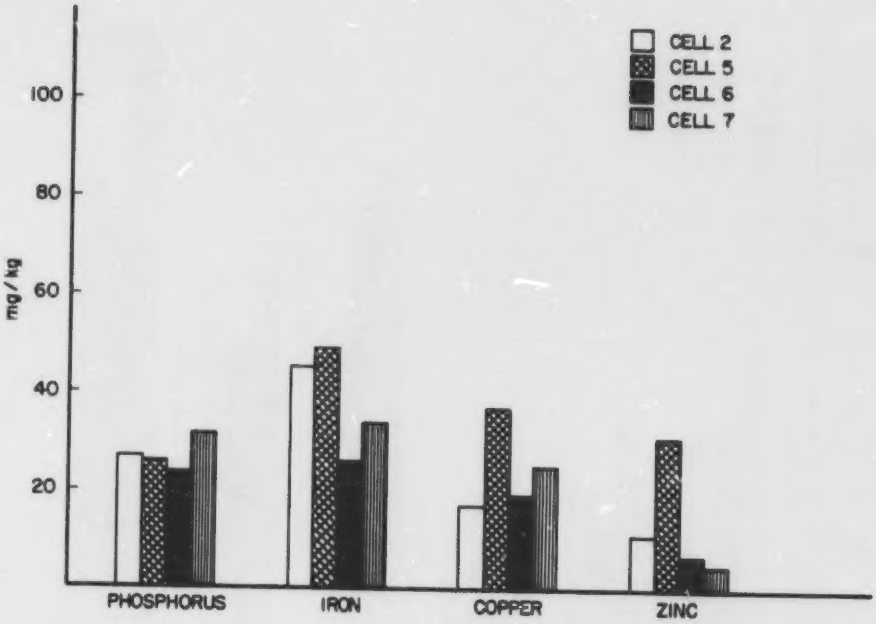

Figure 4 MSW/Sewage Sludge Data

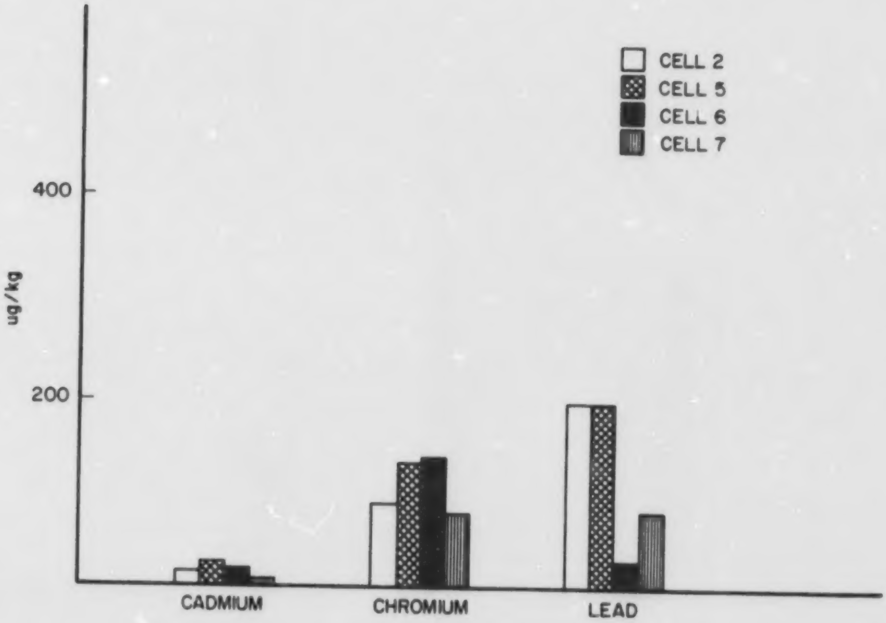

Figure 5 MSW/Sewage Sludge Data

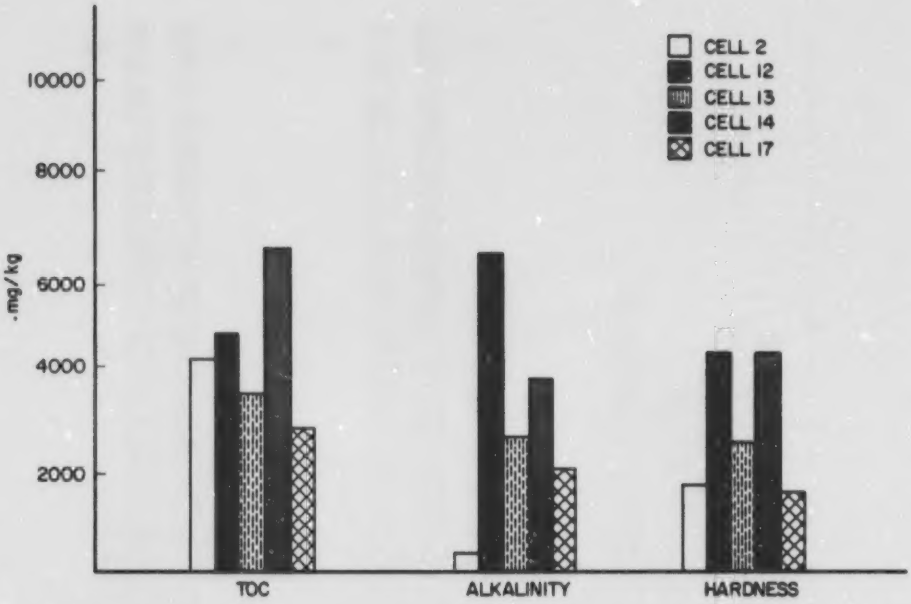

Figure 6 MSW/Industrial Waste Data

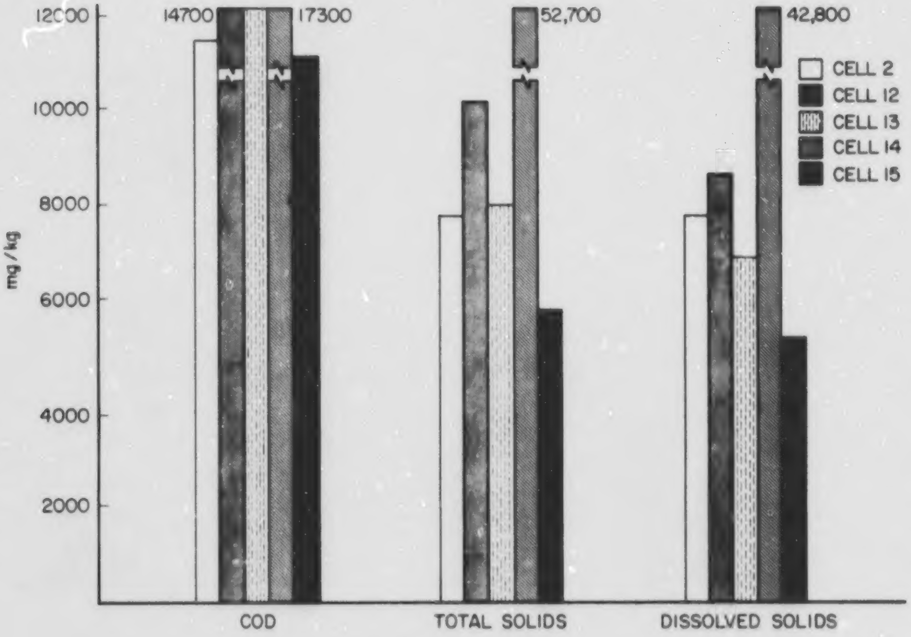

Figure 7 MSW/Industrial Waste Data

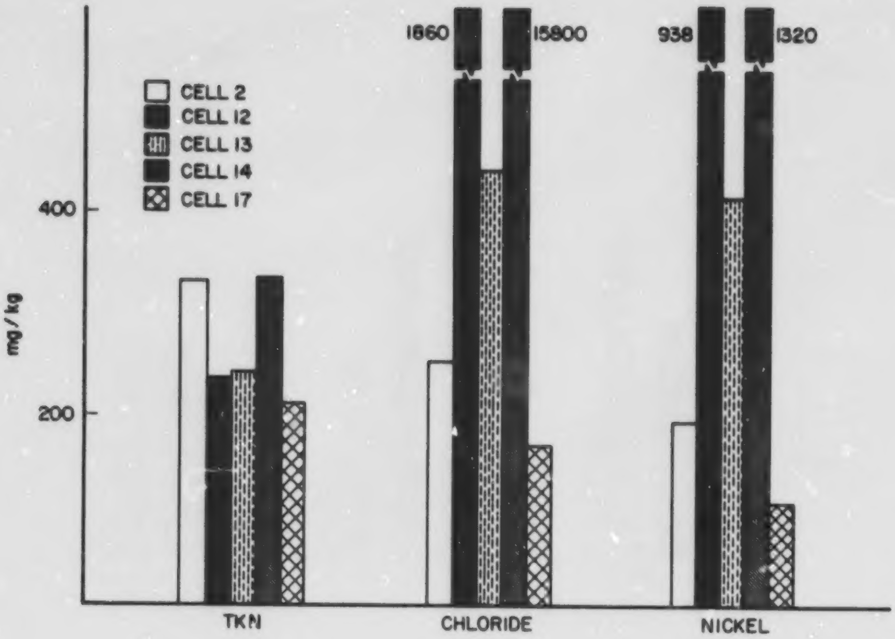

Figure 8 MSW/Industrial Waste Data

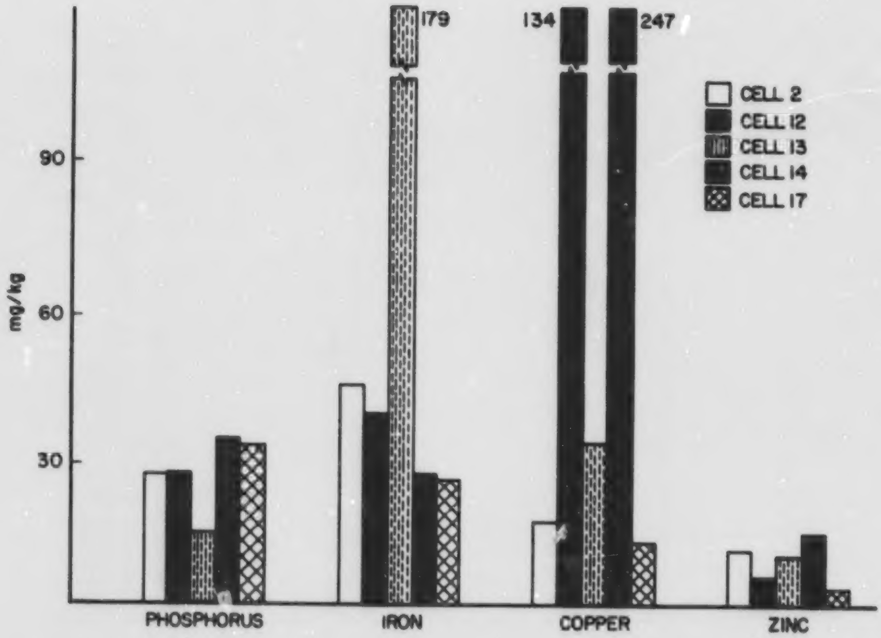

Figure 9 MSW/Industrial Waste Data

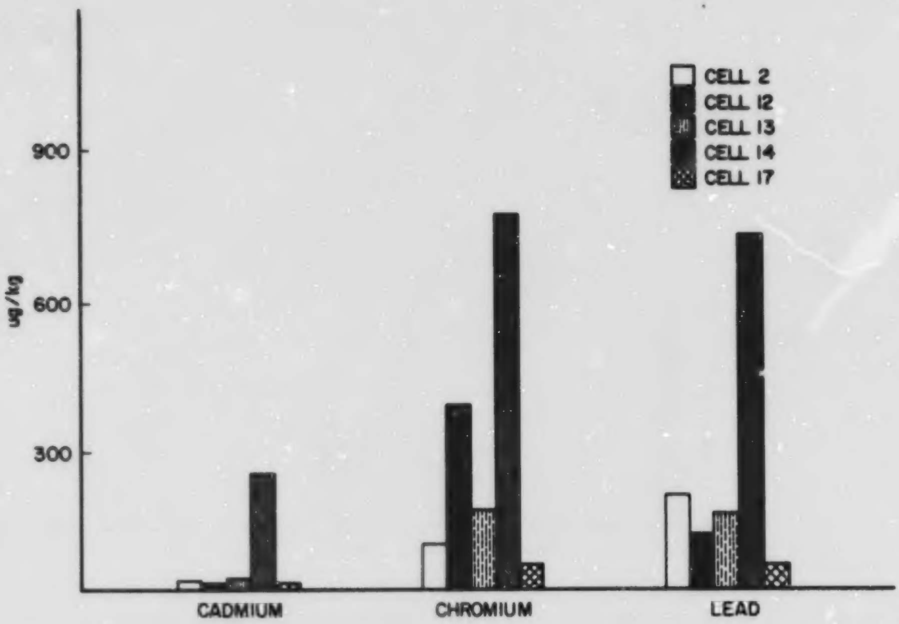

Figure 10 MSW/Industrial Waste Data

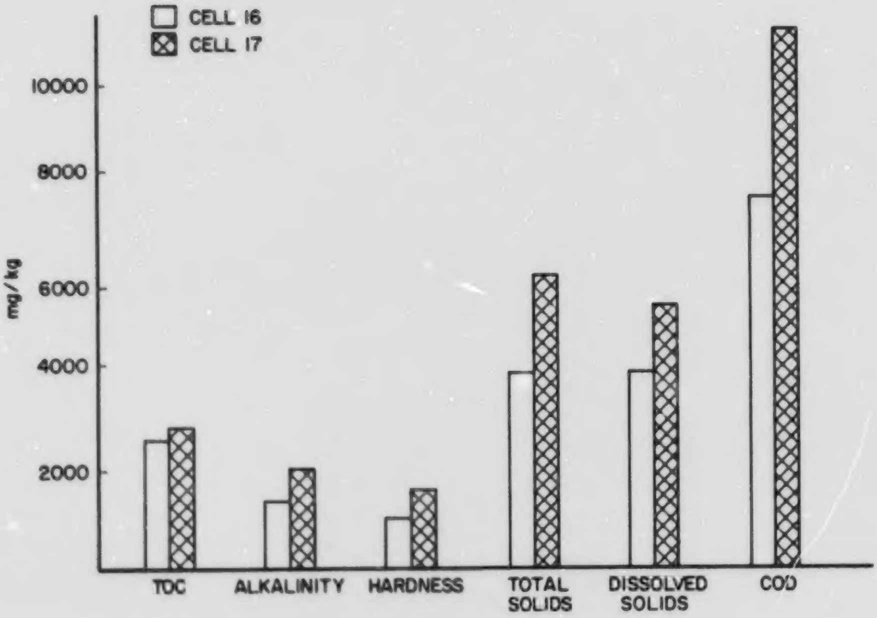

Figure 11 MSW/Industrial Waste Data

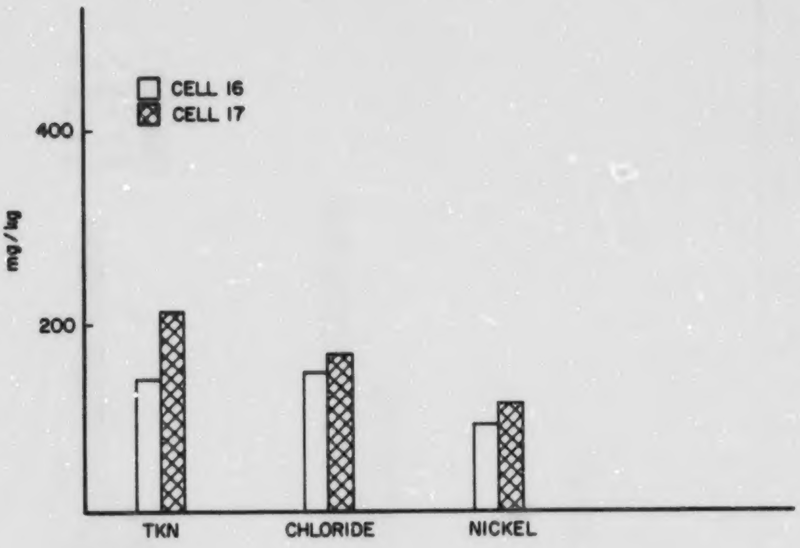

Figure 12 MSW/Industrial Waste Data

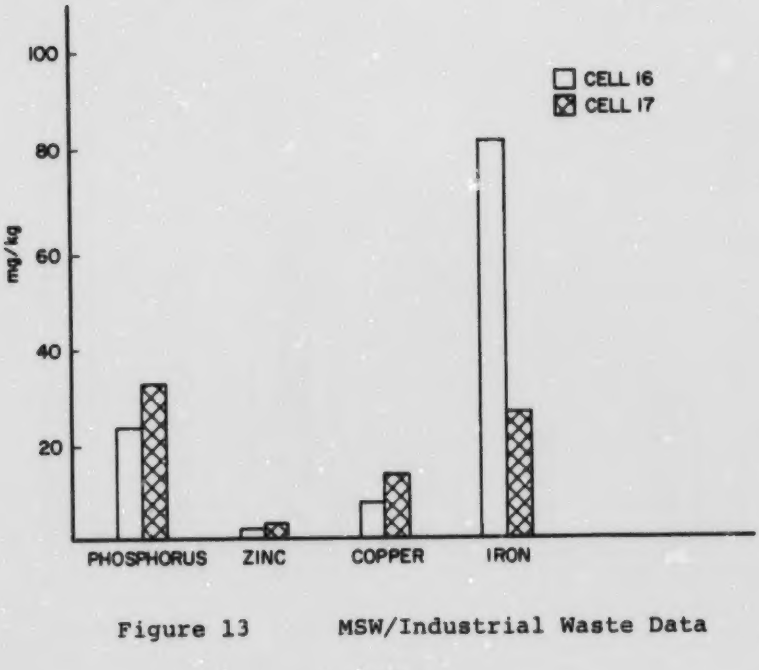

Figure 13 MSW/Industrial Waste Data

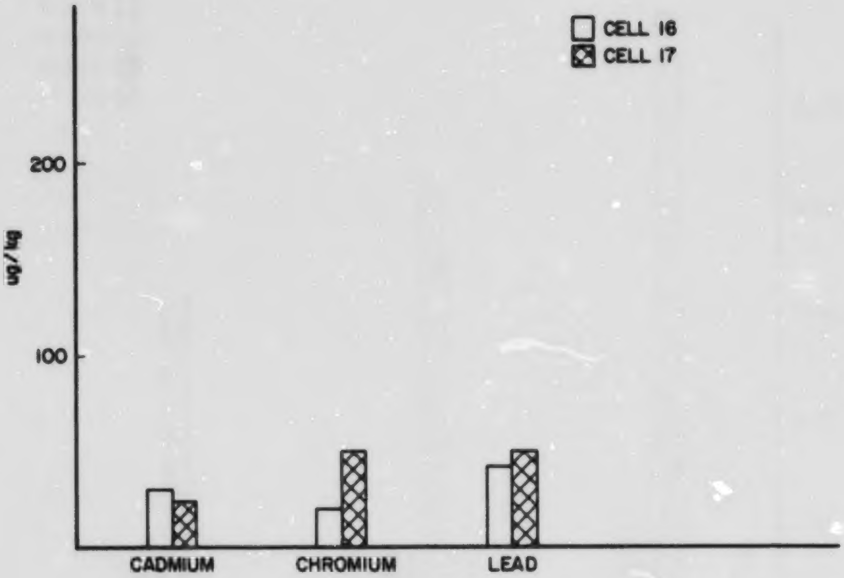

Figure 14 MSW/Industrial Waste Data

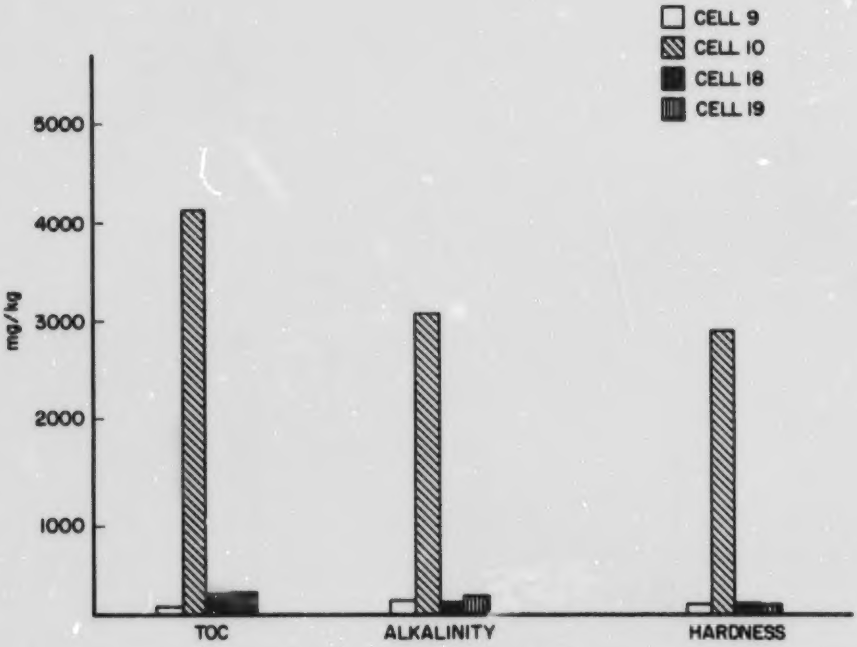

Figure 15 MSW/Industrial Waste Data

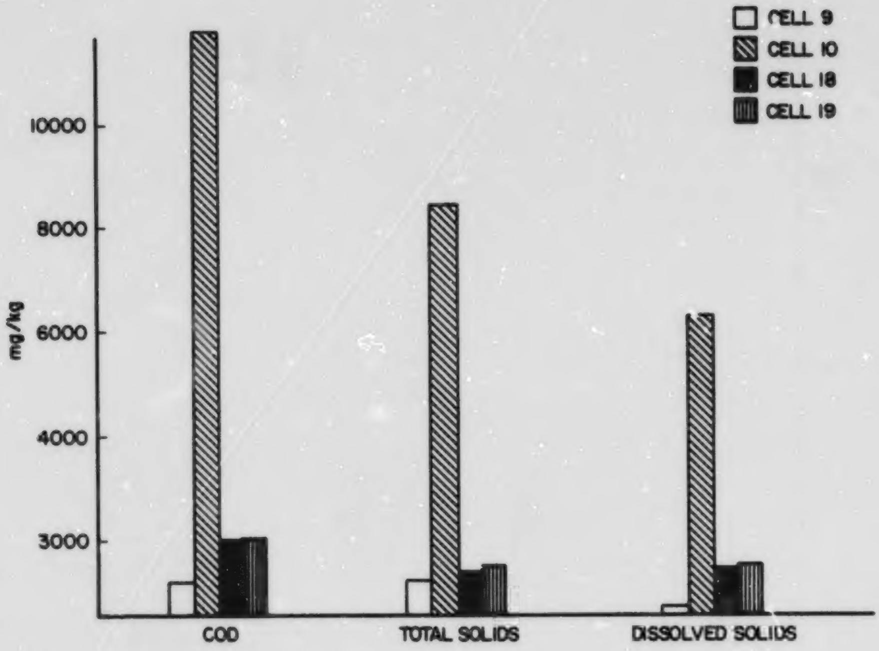

Figure 16 MSW/Industrial Waste Data

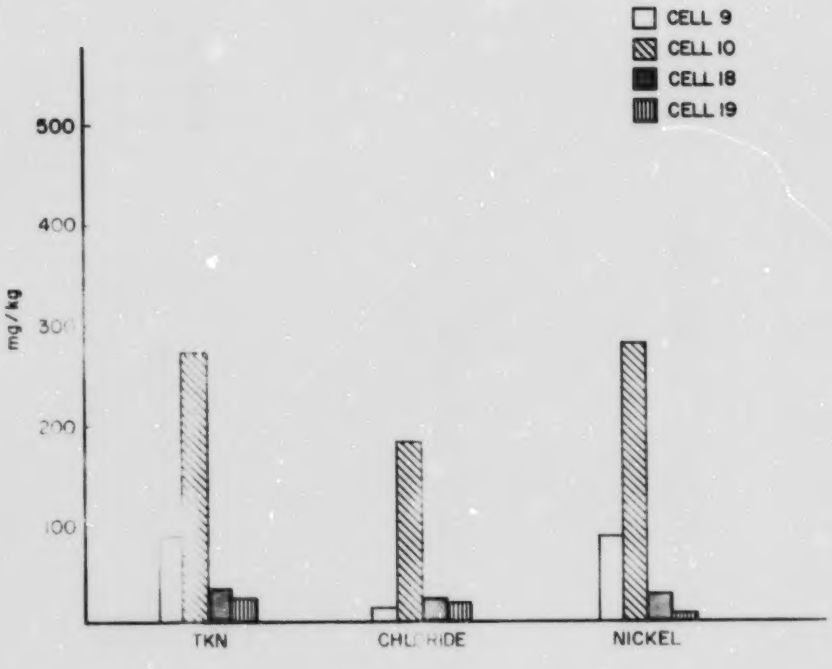

Figure 17 MSW/Industrial Waste Data

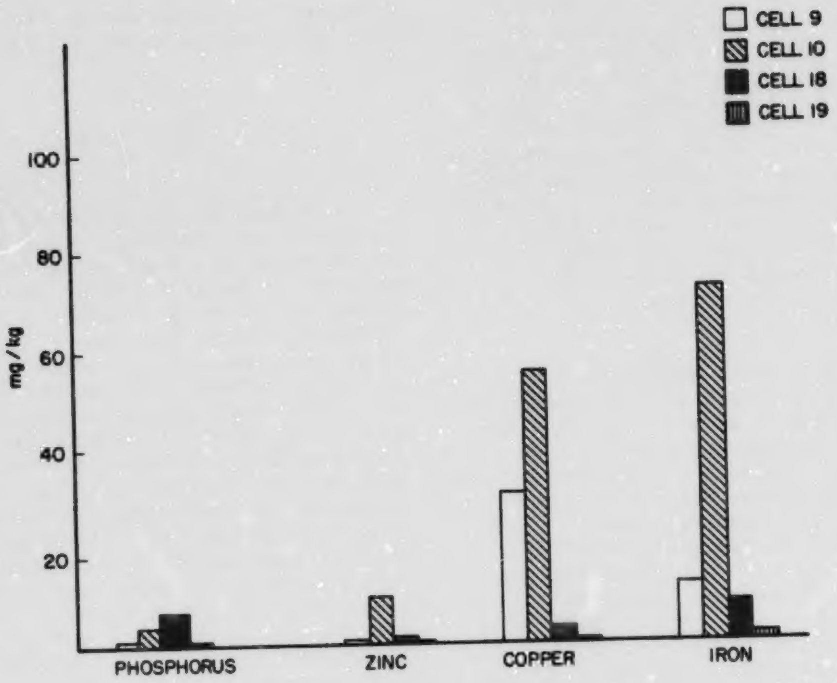

Figure 18 MSW/Industrial Waste Data

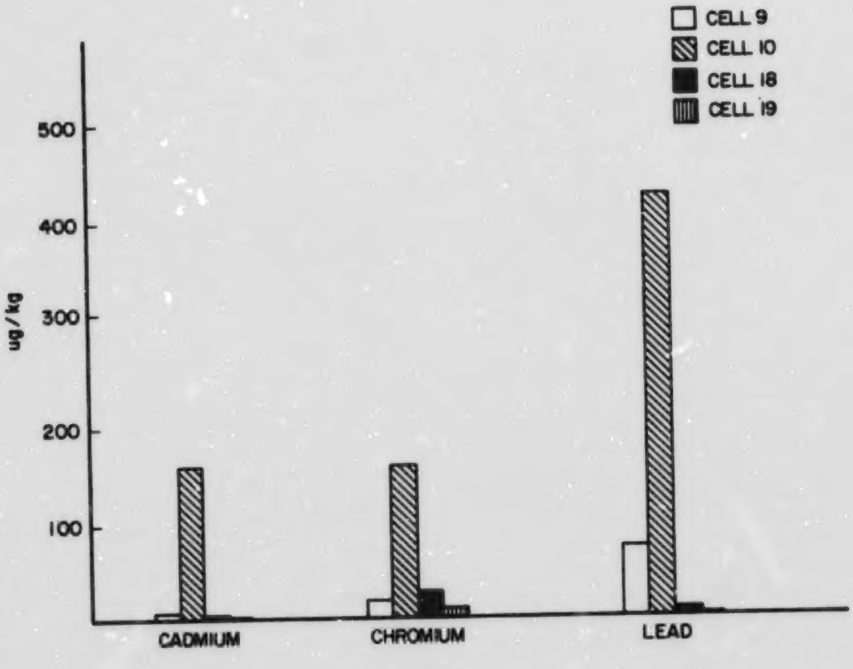

Figure 19 MSW/Industrial Waste Data

the time period discussed in this report, appears to be a serious potential hazard to the surrounding water environment. A comparison of this cell with the control cell containing municipal refuse only indicates that in all parameters the concentrations of leachate pollutants are generally higher. Many of these differences are quite large. Serious consideration of the situation should be made before landfilling this waste.

The test cell containing the solvent based paint sludge additive (cell 17) when compared to the outside cell containing municipal refuse only (cell 2), exhibited test parameter concentrations generally lower than the control cell. This would appear to indicate that the solvent based paint sludge has an inhibitory effect on leachate pollutant concentration. However, as cell 2 is located inground in the outside environment and cell 17 is located in the high bay building the noted inhibitory phenomenon could possibly be more a temperature effect than a coating effect of the paint sludge additive. A comparison with interior municipal refuse only (cell 16) only serves at this time to complicate the issue as cell 17 exhibits generally higher cumulative leachate pollutant concentrations than does cell 16. It is also important to note that in comparing cell 2 (outside) with cell 16 (inside) it was noted that the inside cell (#16) was generally lower than the outside cell (#2) in cumulative leachate concentrations, thus indicating a inhibitory effect possibly due to environment temperature differences. These observations produce the following question in regard to the MSW/Solvent Based Paint Sludge System. Is the fact that cell 17 generally exhibits higher cumulative pollutant concentrations than cell 16 but less than cell 2 indicative of an environmental temperature effect, the result of a coating process by the paint sludge, or some combination of the two? The resolution of this situation will necessarily be part of the continued program as findings to date do not provide satisfactory answers.

GAS DATA

In any study concerning the landfill environment, the collection of data on the different gases generated is desirable though not always easy when coupled with other studies. Such was the situation in this program. Plans were made to collect information on the effects of industrial waste co-disposal upon gas generation. A recurring gas leakage problem thwarted these efforts in the majority of cells located underground. However, the interior cells were successfully sealed and gas data was collected and analyzed. Those results are presented here not because they are associated with the co-disposal of hazardous wastes but because of their potential interest to landfill investigators.

In their work on landfill gas composition Rovers and Farquhar[2] predict a composition versus time curve following a pattern as shown in Figure 20. This plot is based upon the "assumptions that, upon placement, subsequent aeration of the refuse does not occur and that conditions within the decomposing refuse are sufficient to encourage and to sustain CH_4 production". This is a valid assumption in theory but is a condition which does not necessarily exist in an actual situation. In their reports, Rover and Farquhar[2] state the infiltration from melting snow and ice caused an inhibition of the CH_4 forming bacteria, the cause of which was not known. They also stated that aeration of the refuse from air drawn in by the infiltrating water may also have disrupted CH_4 production. The authors of this study also feel that the lowered CH_4 production was very likely caused by an inhibition of the CH_4 forming bacteria. However, data obtained in this study appear to indicate that the aeration which

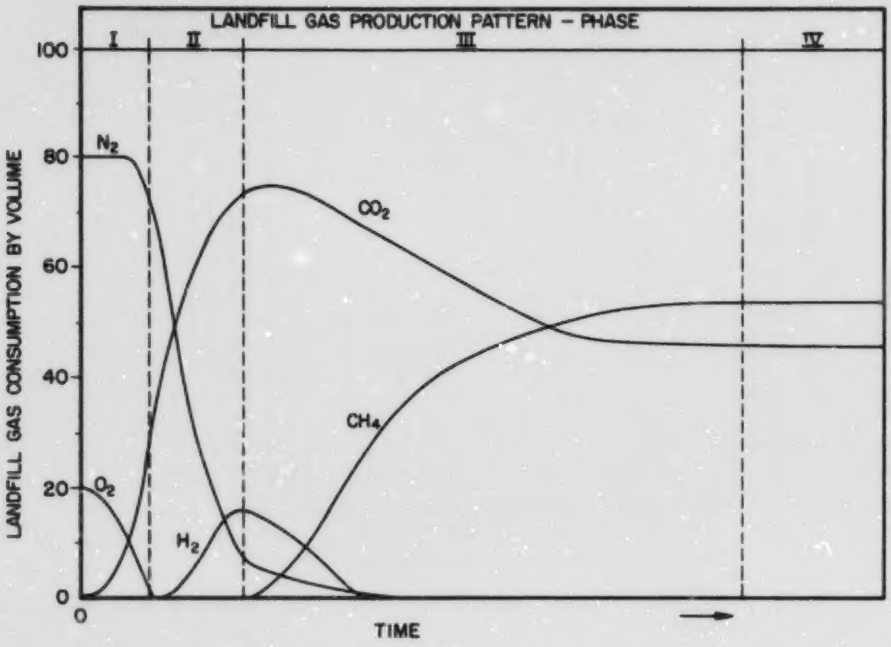

Figure 20 Sanitary Landfill Gas Production Pattern

caused the inhibition had as its possible source the dissolved oxygen content of the infiltration water rather than any air drawn in by the water addition. This possibility is borne out by other researchers.[2,3] A reasonable correlation was noted between water addition and the cyclic methane production found in both this study and another similar one being conducted at another site in Franklin, Ohio. The observation is made that the aerobic bacteria systems and the anaerobic systems which produce methane in a real world situation do not necessarily develop in a hard and fast time frame such as that postulated in theory by Rovers and Farquhar[2]. In fact, these bacterial systems are in a dynamic state of flux and are dependent upon outside sources of influence to determine which is dominant at a given time. In the case of a landfill this outside influence appears to be caused to a great degree by the infiltration of water containing dissolved oxygen. The availability of oxygen is the determining factor of whether biological decomposition is by aerobic or anaerobic organisms.[4] In this study it was concluded that the addition of water containing a high concentration of dissolved oxygen caused a shift from anaerobic to aerobic bacterial dominance, thereby serving to cause an overall low concentration of CH_4 to be produced. (Figures 21-26)

ACKNOWLEDGEMENT

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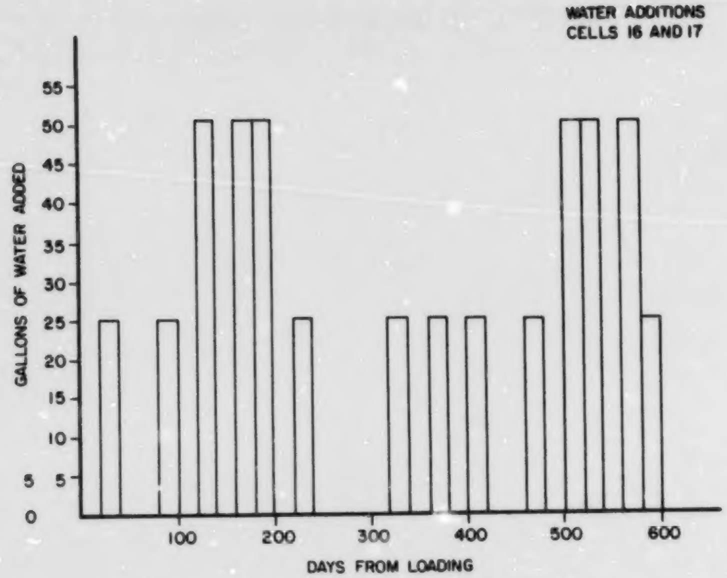

Figure 21 Water Addition Data - Cells 16 and 17

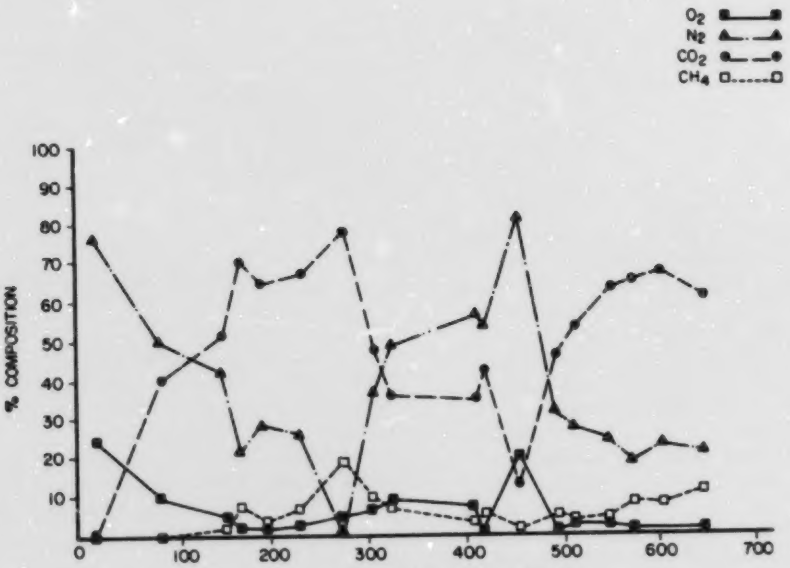

Figure 22 Cell 16 Gas Composition Data

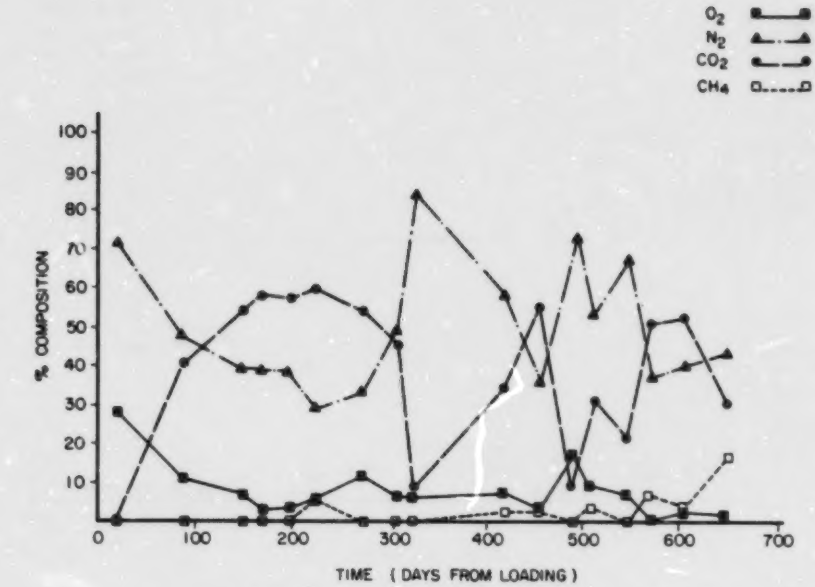

Figure 23 Cell 17 Gas Composition Data

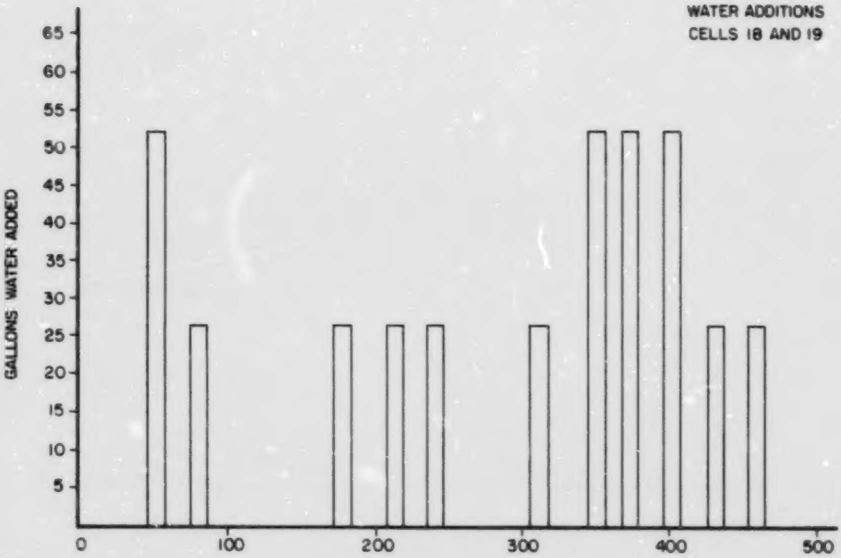

Figure 24 Water Addition Data - Cells 18 and 19

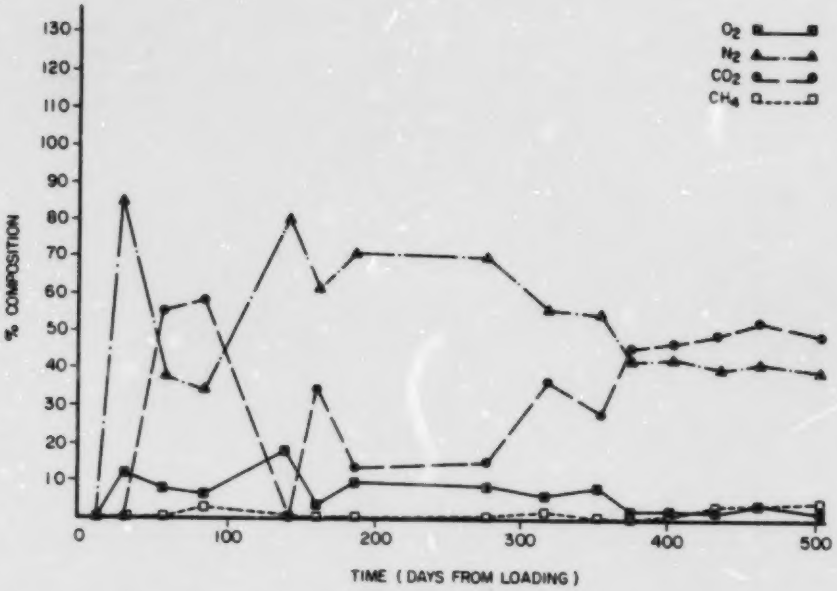

Figure 25 Cell 18 Gas Composition Data

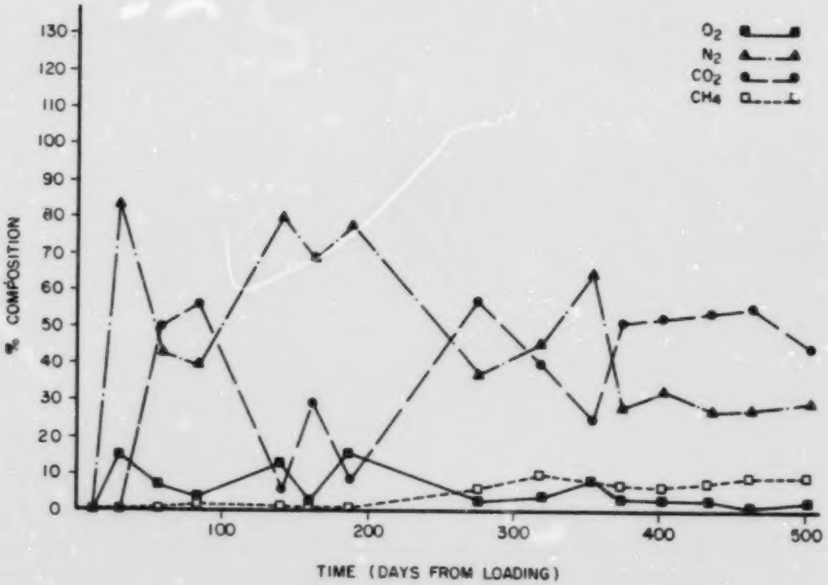

Figure 26 Cell 19 Gas Composition Data

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ACCELERATED TESTING OF WASTE LEACHABILITY AND CONTAMINANT MOVEMENT IN SOILS

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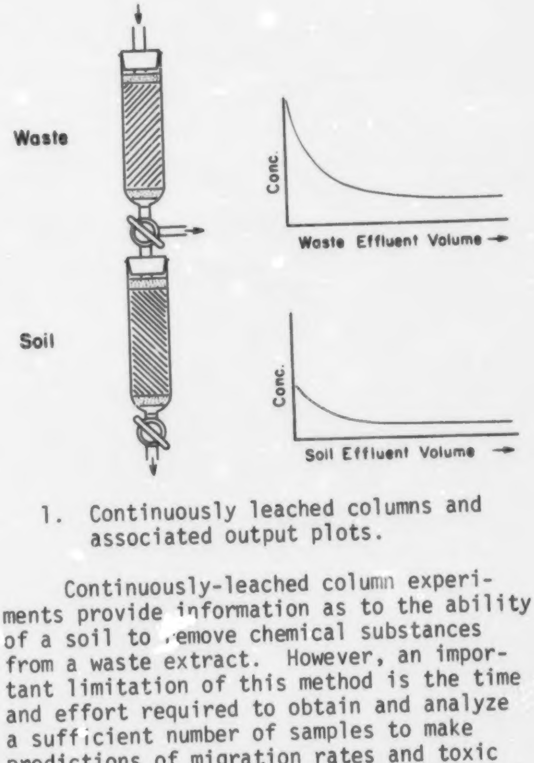
ABSTRACT

Sequential batchwise extractions of waste and soil can be used to simulate continuously leached columns. Successive extracts of a waste (which change in composition as the waste is depleted) are used to challenge a sequence of three soil batches that are graded in size to allow taking samples for analysis between each step. By the proper choice of plotting parameters, a time scale can be related to the cumulative extraction volumes. The described procedure allows simulating years of field leaching in a few weeks of laboraatory extractions.

INTRODUCTION

The ability of a soil to retard the movement of chemical substances leached from a waste is one of the important factors in designing and selecting a waste disposal site. Unless the soil can retard waste leachate movement or remove the hazardous materials from the leachate, contamination of ground-water may result. The chemical and physical composition of a soil are the primary factors determining the soil's effectiveness for shielding the soil's effectiveness for shielding ground-water from contamination. However, the composition of the waste, environmental factors such as annual precipitation, and the geology of the area, are also very important. These factors may be of equal or greater importance than the soil composition if a very soluble waste containing large quantities of toxic substances is improperly disposed of.

The migration of chemical substances through soil is usually studied in the laboratory using columns packed with soil to a predetermined bulk density. These soil columns are challenged with a solution extracted from a waste by water or some other solvent such as municipal landfill leachate, or the soil is treated with simple solutions of the ion under study. (A useful configuration is shown in Figure 1, along with illustrative plots of the data obtained.)



1. Continuously leached columns and associated output plots.

Continuously-leached column experiments provide information as to the ability of a soil to remove chemical substances from a waste extract. However, an important limitation of this method is the time and effort required to obtain and analyze a sufficient number of samples to make predictions of migration rates and toxic hazards. This usually requires months and may even take years, depending upon the flow rate of the leaching solution through the columns. The information obtained from relatively short-term column studies cannot be expected to describe what will occur during years of leaching.

The desirability of maintaining a uniform flow through waste or soil columns is shown by studies which indicate that the extraction of the waste and the removal of some compounds from the leachate by the soil is flow-dependent (1,2). Maintaining the flow rate at a constant, preselected value is usually attempted either by restricting the flow rate of the effluent from the soil column, by regulating the head pressure of the liquid above the waste, or by using precise, flow-regulating pumps. The regulation is not easy, so the columns must be carefully monitored. (Soils containing a large sand fraction allow nearly free flow of the waste leachate while soils containing large amounts of clay and silt require a large head pressure in order to obtain a reasonable flow.)

When setting up experiments of this type, any investigator is faced with the problem of selecting values for each experimental parameter such as leaching solvent flow-rate, head-pressure, soil bulk density, column diameter, waste-to-soil ratio, etc. The choice of these values may not all be entirely arbitrary, but a given set will yield results which probably apply only to that particular combination of conditions, and the experiment may not be very useful for making general predictions. By having a more rapid and more flexible experimental approach, a wider range of conditions can be investigated within the framework of factorial experiment designs which do allow making predictions even in the presence of interaction between multiple variables. (Interaction exists when the effect of one factor is dependent upon the level of another factor. This introduces error into the results of classical, vary-one-factor-at-a-time experimentation.) A fast method also allows making timely determinations, on demand, for each specific situation.

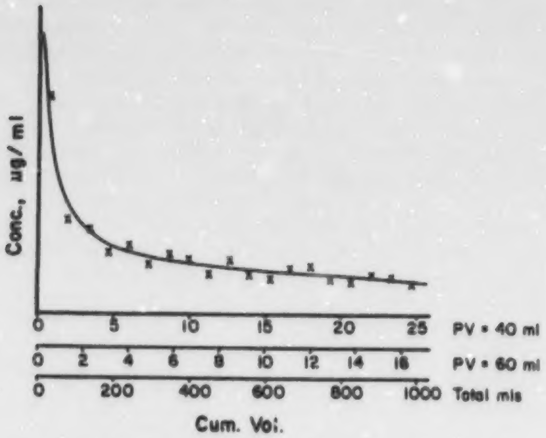
Recently, our laboratory investigated the leachability of certain toxic metals from a number of industrial wastes and studied the migration of these metals through soils. We used a batch method to rapidly screen soils for their ability to remove these metals from the waste leachate (3). This information was then used to select soils for more detailed column studies. While examining the data, it became apparent that properly designed batch studies of both wastes and soils could provide much of the same information obtained from column studies. However, no adequate information was available as to the correlation between batch extractions and continuously-leached columns of wastes and soils. Samples of industrial wastes used in the previous studies with continuously-leached columns were therefore leached using a serial batch extraction procedure. It was found that the weights of toxic metals extracted from the wastes batchwise compared well to the column leaching (4). Besides this, the results were obtained by the serial batch extraction method in only a small fraction of the time required by the column method. The serial batch method is experimentally much simpler, and it permits the rapid investigation of the effect of a wide variety of additional environmental factors, such as freeze/thaw and drying/resaturating cycles.

Other investigators have used batch soil methods to study the removal of certain chemicals from waste extracts or municipal landfill leachate (5-6) and obtained results that compared with soil columns for their experimental conditions. However, their experiments either did not allow for the changes in the waste extract composition as the waste is depleted, for the further change as the extract contacts each increment of soil, and/or for the continually changing conditioning of each increment of soil, a change which depends both upon the leaching time and the number of soil increments above the one in question.

This paper reports some further refinements of the serial batch procedure for evaluating waste leaching and presents the extension of the procedure to studying the removal of metal ions by soil.

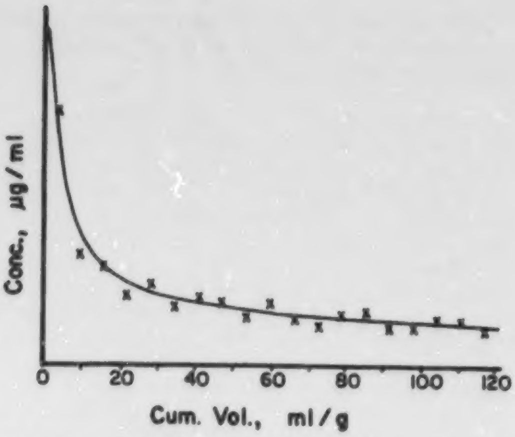
CORRELATING CONTINUOUS AND BATCHWISE LEACHING

The data obtained from continuously-leached columns may be presented in several ways. One technique is to plot the concentration of the chemical of interest found in the waste or soil column sample versus the cumulative volume through the column. The common way of expressing the cumulative volume is to use the cumulative pore volume calculated for the type and weight of soil employed. However, changing the type or weight of soil will change the scale of the cumulative volume axis when pore volume is employed. Figure 2 is an example showing the difference obtained with pore volumes of 40 and 60 mls. The corresponding total volume in milliliters is appended for comparison.



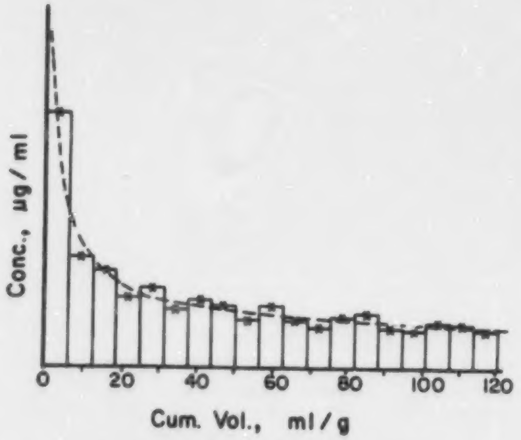
2. Differences in scales used to plot cumulative volume.

It often is not practical or possible to determine a pore volume for a waste due to its physical form (heterogeneous suspension, liquid, etc). This problem is circumvented by using the soil column pore volume as the measure of liquid volume through the waste. It allows correlating the waste-column output with the soil-column results in a given set of experiments. However, instead of using the soil pore volume as the principle plotting parameter, it is much more flexible to plot the observed concentration of a chemical in an extract versus the cumulative milliliters of leaching solvent per gram of waste or soil, as shown in Figure 3. This makes the scaling independent of soil type, soil sample weight, and waste-to-soil ratio and allows the direct comparison of many different designs of experiments. It normalizes the results so they can be more readily correlated to a range of field conditions. The area under the curve represents the total weight of a chemical extracted per gram of waste or soil.



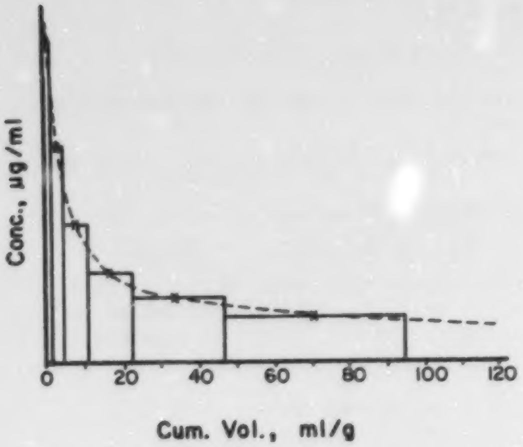
3. Normalization of cumulative volume using milliliters per gram.

Batchwise extractions can be related to continuously-leached columns by recognizing that continuous leaching is equivalent to running a series of discrete extractions spaced by the frequency of collecting the effluent sample. Figure 4 shows that the concentration of the periodic column samples can be plotted to represent the average for that sampling period. Thus, samples from the continuous leaching of a column correspond to sequential batchwise extractions by volumes of extractant equal to the volume passing through a column between the taking of samples.



4. Correlation of batch with continuously leached columns.

When extracting a batch of waste or soil, instead of using the same volume of solvent for each successive extraction, the solvent-to-waste or -soil ratios can be graded in size, as indicated by the extraction volumes pictured in Figure 5. A small solvent-to-solid ratio should probably always be employed for the first extractions; this is usually when the concentration is changing most rapidly, so smaller increments define the curve more accurately. It also is when the soluble species will be the most highly concentrated in the extract and the ionic strength will be at its maximum. Greater dilutions would reduce this, possibly affecting the solubility of other components. After the more soluble components have been extracted, the solvent-to-solid ratio can be greatly increased, thus reducing the total number of extractions required. The further along the cumulative milliliter per gram axis the extraction volumes extend, the longer the period of column leaching the batch work is equivalent to.



5. Graded serial batch extractions.

Batch extractions are rapid compared to letting the liquid percolate through a column. If the volume of liquid used in a batch extraction can be related to the same volume of liquid passing through a waste or soil over a period of time, sequential batch extractions can be the basis for an accelerated testing of wastes and soils. However, the fraction of void space in a soil (the pore fraction) affects the volume of effluent passing through a soil per unit time. The pore fraction can be calculated from the formula

$$PF = 1 - \frac{\rho_b}{\rho_p}, \qquad (1)$$

where:

PF = pore fraction,

ρ_b = bulk density, g/cm^3, and

ρ_p = particle density, g/cm^3.

The pore volume is the total volume of void space in given quantity of soil. This is obtained by multiplying the volume of the soil by the pore fraction

$$PV = (PF)(V), \qquad (2)$$

where: PV = pore volume, cm^3, and
V = volume of soil, cm^3.

To find the pore volume of one gram of soil (which is of interest because the gram is the basis for the normalization employed in this paper), substitute the volume occupied by one gram of soil, as calculated from

$$V = \frac{1}{\rho_b}\ \text{cm}^3, \qquad (3)$$

into equation 2, which yields,

$$PV = \left(1 - \frac{\rho_b}{\rho_p}\right)\left(\frac{1}{\rho_b}\right) \text{cm}^3. \qquad (4)$$

(The pore volume may be corrected for the fact that not all of the liquid contained in the pores is exchangeable with a mass of liquid moving through the soil. This effective porosity is estimated to be 90 percent for most soils(9), so values obtained from equation 4 should be multiplied by 0.90.)

The velocity of a moving liquid front will be related to the volume displaced by the front by first calculating the depth occupied by one gram of soil out of the total weight contained in a cubic centimeter. One gram of soil having a specified bulk density and a cross-section of one square centimeter will have a depth

$$h = \frac{1}{\rho_b}\ \text{cm}, \qquad (5)$$

where:

h = depth, cm.

The time required for a liquid front to pass through one gram of soil having a depth of $\frac{1}{\rho_b}$ cm is

$$T = \frac{\frac{1}{\rho_b}}{v} \text{ days,} \qquad (6)$$

where:

T = time, days, and
v = velocity, cm/day.

Since this gives the time required for a liquid front to pass through one gram of soil at the selected velocity, i.e., the time required to fill the pore volume of one gram of soil, the reciprocal is the number of times the gram of soil is penetrated by a unit volume of liquid. Multiplying this by the pore volume for one gram of soil gives the volume of liquid penetrating the soil at the selected velocity

$$V = \frac{v\ (PV)}{\frac{1}{\rho_b}} \text{ cm}^3. \qquad (7)$$

The time required for any volume of liquid to penetrate the one gram at a selected velocity can be calculated from the equation

$$T = \frac{V}{\frac{v\ (PV)}{\frac{1}{\rho_b}}} \text{ days.} \qquad (8)$$

To illustrate the use of these generalized equations, assume that a soil has a bulk density of 1.6 g/cm^3 and a particle density of 2.65 g/cm^3. (These values are representative of the clays used in the experimental work reported in this paper.) Thus, from equation 1, the pore fraction is

$$PF = 1 - \frac{1.6}{2.65} = 0.40,$$

and the pore volume per cubic centimeter is

$$PV = (0.40)(1.0) = 0.40 \text{ cm}^3.$$

The volume occupied by one gram of soil is therefore

$$V = \frac{1}{1.6} = 0.625 \text{ cm}^3,$$

and the pore volume for the one gram of soil is

$$PV = \left(1 - \frac{1.6}{2.65}\right)\left(\frac{1}{1.6}\right) = 0.248 \text{ cm}^3.$$

Assuming a 90 percent effective porosity,

$$PV = 0.248 \times 0.90 = 0.223 \text{ cm}^3.$$

If a liquid penetrates this soil at a velocity of 1×10^{-5} cm/sec (which is 0.864 cm/day), one milliliter of liquid will penetrate one gram of soil in

$$T = \frac{1}{\frac{(0.864)(0.223)}{\frac{1}{1.6}}} = 3.24 \text{ days.}$$

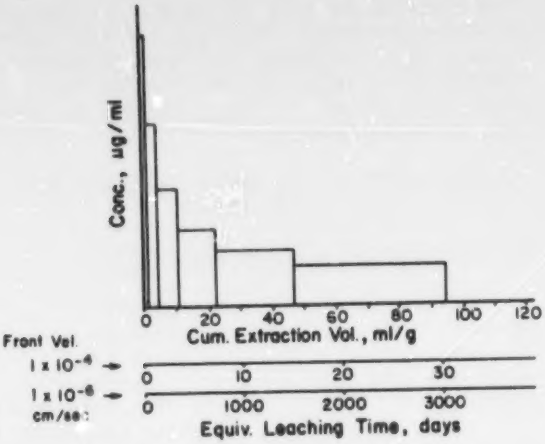
Thus, an extraction with 2 milliliters per gram of soil is equivalent to 2 x 3.24 = 6.48 days of penetration in the field or in a column. Table 1 lists the liquid-to-solid ratios we employed, together with the cumulative volumes and equivalent exposure times for liquid front velocities of 1×10^{-4}, 10^{-5}, and 10^{-6} centimeters per second through a typical clay. This correlation is displayed graphically in Figure 6.

The velocity of the liquid through a soil underlying a specific waste-disposal site must be determined experimentally to be able to choose the correct correlation. However, the flow-rate determining factor will often be the penetrability of the layer of waste. Table 1 also applies to the leaching of waste because the volume of

TABLE 1. Correlation Between Extraction Volume and Penetration Time

Extraction Number	Water Added, ml/g	Cumul. ml/g	Equivalent Days of Penetration[a] 10^{-4}	10^{-5}	10^{-6} cm/sec
1	2	2	0.65	6.5	65
2	3	5	1.62	16.2	162
3	6	11	3.56	35.6	356
4	12	23	7.45	74.5	745 (2.0 yr)
5	24	47	15.2	152.	1520 (4.2 yr)
6	48	95	30.8	308.	3080 (8.4 yr)
7	96	191	61.9	619. (1.7 yr)	6190 (16.9 yr)

[a] At the specified liquid front velocity through a soil having a pore volume of 0.223 ml/g.



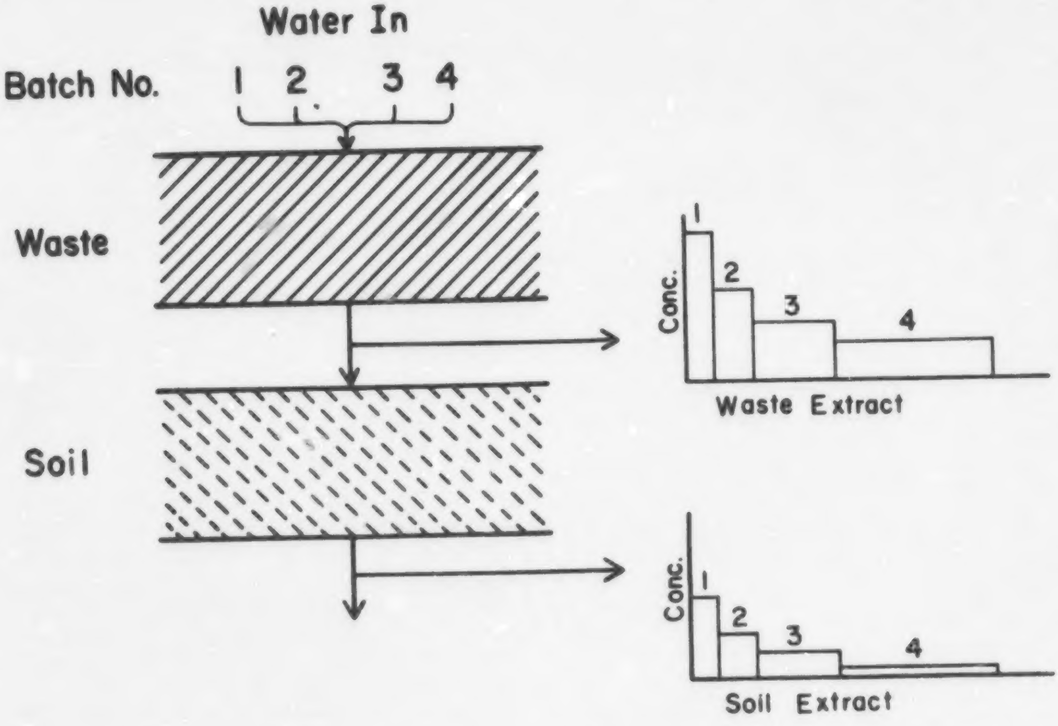
6. Relating batch volumes to leaching times for soils having a pore volume of 0.223 ml/g.

liquid through a column of waste will be the same as through the soil beneath it, as previously discussed.

THE GRADED SERIAL BATCH EXTRACTION OF WASTES AND SOILS

The waste composition changes as components are leached from the waste. Each succeeding portion of extract will therefore generally have a different composition as shown in Figure 7. Besides being challenged by a changing solution, the soil's ion-removal characteristics continually change with time as the soil becomes conditioned and loaded by the passage of waste extracts. Since each portion of waste is changed by passage through a segment of soil, the conditioning each succeeding segment of soil receives is different and each segment therefore may remove different proportions of the various ions present in the waste extract. So although the soil segments start out the same, in effect they become different soils due to the passage of the different waste extracts.

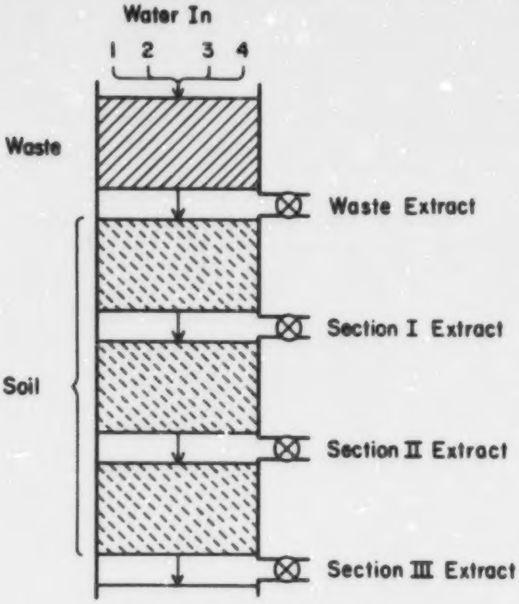
The soil removes ions from the waste, but the waste extract can also displace ions from the soil. In addition, soil can pick up a specific ion from a waste solu-



7. The results of challenging soil with successive extracts of waste.

tion of one composition and then give it up again as the liquid composition changes. The soil may also give up ions later because of intervening conditioning of the soil by the passage of the changing waste extract solution.

If extract samples were taken within a layer of soil, it would be possible to study this dynamically-changing situation. This can be accomplished by placing sampling ports in the side of a soil column, as shown in Figure 8. The same results can be attained in a shorter time with far fewer equipment difficulties by putting waste extracts on successive batches of soil and taking a sample after each extraction. A batch of soil then will represent a segment of soil from a soil layer.



8. Challenging multiple soil segments with successive extracts of waste.

Normally, the distribution of substances retained by the soil column is determined after leaching is concluded by sectioning and analyzing the soil column. But, this serial batch approach, with sampling between batches of soil, allows perceiving what is happening within a bed of soil and provides data which could allow extrapolating to the effect of thicker strata--something which cannot be done with validity from experiments with only a single layer, or from experiments which use simpler conditions. It is re-emphasized that batchwise testing also yields its information in a small fraction of the time required by columns or field studies.

APPLICATION OF THE BATCH TECHNIQUE TO INDUSTRIAL WASTES

Characteristics of Waste and Soils

We have applied this procedure to seven different industrial wastes so far. The results from a zinc-carbon battery waste are presented here to illustrate the method. This waste consists of broken-open reject batteries. Table 2 shows the waste battery composition per 1000 kg of batteries produced. (Approximately one percent of the batteries produced are rejected.) The extract samples were analyzed to determine the amount of each metal present at every state of the batch tests.

TABLE 2. Composition of Zinc-Carbon Battery Waste per 1000 kg Batteries Produced (10)

Constituent	Waste Factor (kg/1000 kg)
Mercury	0.0073
Zinc	3.812
Zinc Chloride	0.248
Manganese Dioxide	6.147
Cadmium	0.00027
Lead	0.00031

Three soils were investigated for their ability to remove the metals of interest from extracts of the zinc-carbon batteries. The soils chosen were Chalmers (a gray, silty, clay loam from Indiana, a Mollisol), Davidson (a red clay from North Carolina, an Utisol), and Nicholson (a yellow, silty, clay from Kentucky, an Alfisol).

These soils were selected because of differences in their chemical properties and clay mineralogy. Table 3 shows that Chalmers and Nicholson soils have similar surface areas but significantly different cation exchange capacities. In addition, the clay mineral composition (< 2 micron separates) are much different. The Chalmers clay composition is largely montmorillonite, with small amounts of vermiculite, chlorite, and kaolinite. The Nichol-

TABLE 3. Some Physical and Chemical Properties of Soils Used in this Study (11)

Soil	Soil Paste pH	Cation Exchange Capacity, meq/100 g	Surface Area, m^2/g	Free Iron Oxides, Percent	Texture		
					Sand, Percent	Silt, Percent	Clay, Percent
Chalmers	6.6	26	125.6	3.1	7	58	35
Davidson	6.2	9	51.3	17.0	19	20	61
Nicholson[a]	5.0	37 (?)	120.5 (?)	5.6	9	31	60

[a] These values, obtained from the soil we used, show that it differs from Fuller's (11) sample, which had a pH of 6.7. The CEC and surface areas listed are for his sample, which was 49% clay, so our values for these would be somewhat higher.

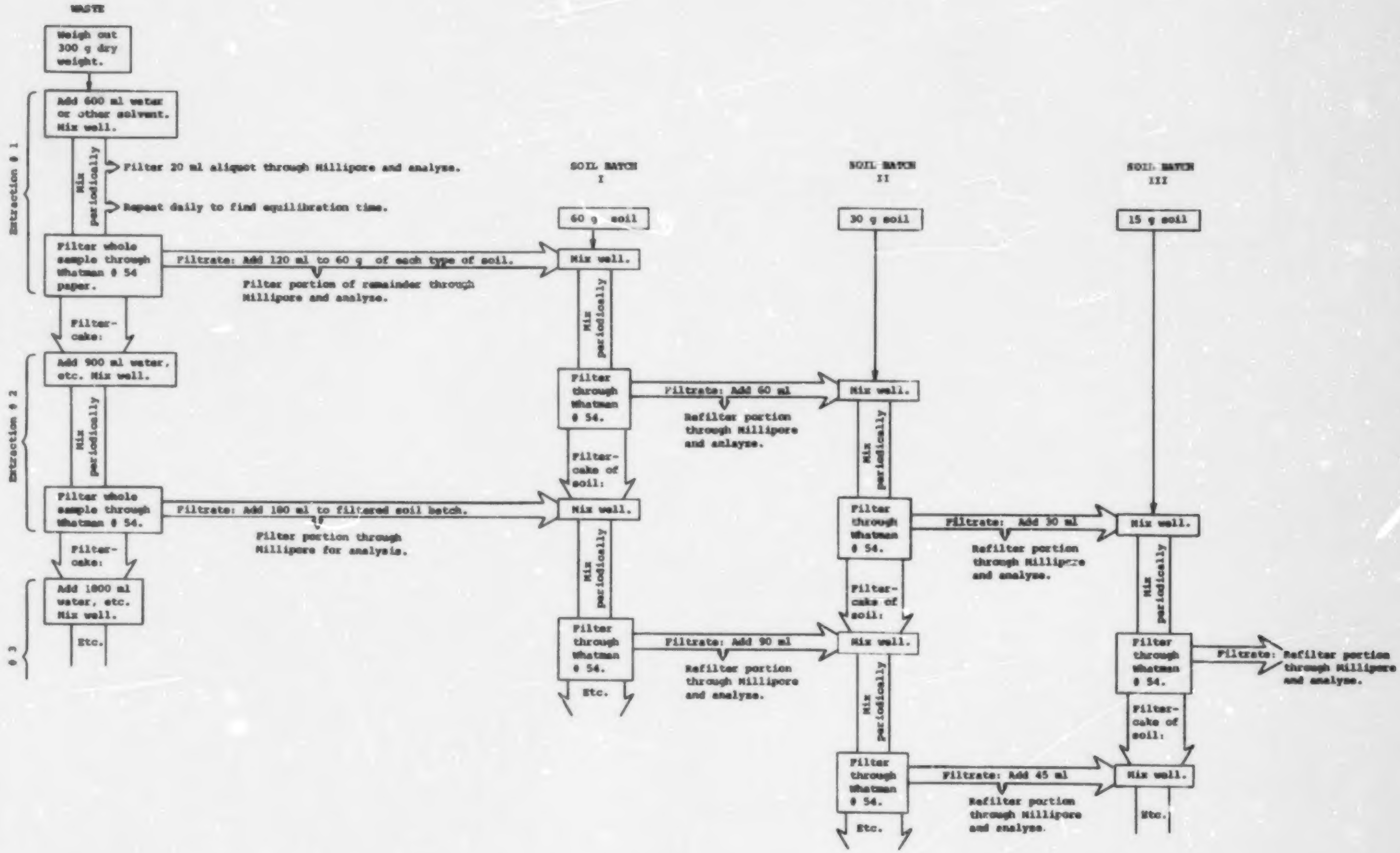
TABLE 4. Specifications for Serial Batch Extractions

Extraction Number	Water Added, ml/g	Volume of Water, ml, Extracting 300 g Waste	Volume of Filtrate Onto a Soil		
			I 60 g Soil	II 30 g Soil	III 15 g Soil
1	2	600	120	60	30
2	3	900	180	90	45
3	6	1,800	360	180	90
4	12	3,600	720	360	180
5	24	7,200	1,440	720	360
6	48	14,400	2,880	1,440	720
7	96	28,800	5,760	2,880	1,440

son clay faction is predominately vermiculite with only a trace of mica and kaolinite. In contrast, Davidson soil has a low surface area and cation exchange capacity. The clay is predominately kaolinite but this soil contains a high percentage of hydrous oxides of iron. It has been shown that iron oxides play a major role in heavy and trace metal removal [12] .

The Procedure Employed

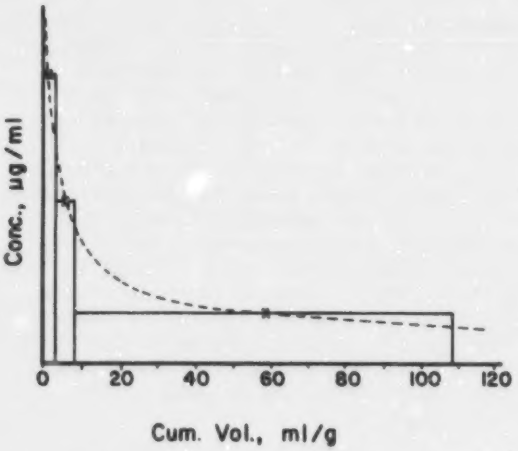
A sequence of seven extracts was made from waste zinc-carbon batteries. Four batteries were weighed and placed in two-quart, wide-mouth screw-cap jars. (Although it was not done with the batteries, ordinarily a sample of waste is dried to determine moisture content, then sufficient undried sample is weighed to give 300 grams dry weight. Drying the sample could affect hydrated species and drastically reduce the solubility. If the waste had supernatant water, the volume of the water was considered as part or all of the first extract.) Appropriate volumes of water were added for each extraction to produce the liquid-to-solid ratio given in the second column of Table 4. The bottle was shaken gently 4 or 5 times daily (Continual mechanical shaking was not used because of concern that it might abrade the waste agglomerates, making them more susceptible to extraction). The time required to reach equilibrium was determined by periodically withdrawing an aliquot for analysis; 24 hours is adequate for most wastes of small particle size, 72 hours was required for the first battery extraction, 48 hours for the remainder. At the end of the extraction period, the mixture was filtered under vacuum using a hardened filter paper (such as Whatman 54) in a Buchner funnel. An aliquot of approximately 20 milliliters was withdrawn for metals analysis and filtered through a 0.5 μ Millipore filter to remove fine particles which might have by-passed the filter paper to possibly dissolve when the sample was acidified. (After measuring conductance and pH, one percent


WASTE
Weigh out 300 g dry weight.
Add 600 ml water or other solvent. Mix well.
Extraction # 1
Mix periodically
Filter 20 ml aliquot through Millipore and analyse.
Repeat daily to find equilibration time.
Filter whole sample through Whatman # 54 paper.
Filtrate: Add 120 ml to 60 g of each type of soil.
Filter portion of remainder through Millipore and analyse.
Filter-cake:
Add 900 ml water, etc. Mix well.
Extraction # 2
Filter whole sample through Whatman # 54.
Filtrate: Add 180 ml to filtered soil batch.
Filter portion through Millipore for analysis.
Add 1800 ml water, etc. Mix well.
# 3
Etc.
SOIL BATCH I
60 g soil
Mix well.
Filter through Whatman # 54.
Filter-cake of soil:
Filtrate: Add 60 ml
Refilter portion through Millipore and anlayze.
Filtrate: Add 90 ml
Refilter portion through Millipore and analyze.
SOIL BATCH II
30 g soil
Filtrate: Add 30 ml
Filtrate: Add 45 ml
SOIL BATCH III
15 g soil
Filtrate: Refilter portion through Millipore and analyze.

9. Flow chart for graded serial batch extractions.

concentrated nitric acid was added to the filtrate to inhibit precipitation while standing.) The solid waste residue was transferred back to the jar and mixed with the volume of water specified for the next batch. The flow-chart of Figure 9 outlines the sequence of operations.

In the procedure detailed here, the liquid-to-solid ratio was continually increased to further accelerate the testing--the volume of each extraction after the second one was made double the one before, which redoubles the time represented by that extract. With some wastes, adequate results may be obtainable by using very large volumes right from the first (or one or two extractions using small liquid-to-solid ratios, followed by a very large one as shown in Figure 10, but this would have to be checked for each kind of waste by comparison with the more conservative series of extractions utilized in Table 4. However, such a procedure would allow rapid simulation of long leaching periods and could be useful in the routine monitoring of variations in waste composition and leachability(4).



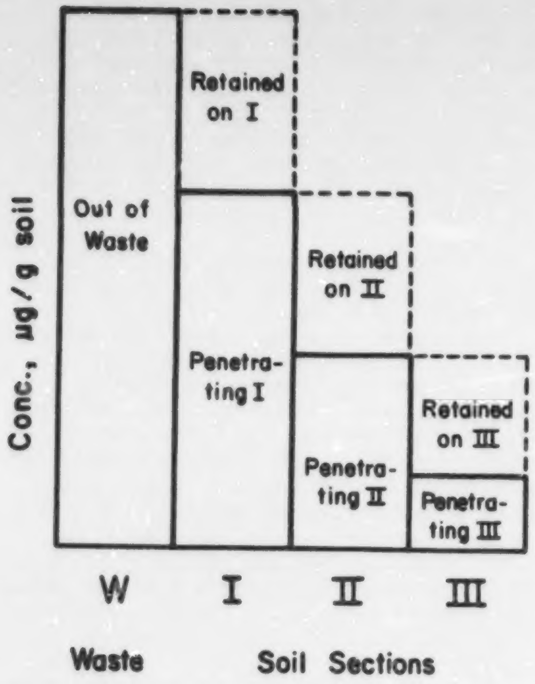
10. Making a rapid estimate by extracting with 3, 5, and 100 milliliters per gram.

The filtrate resulting from each sequential extraction of the waste was mixed with the first of three batches of each kind of soil. The weights of soil used were 60, 30, 15 grams, representing section I, II, and III, respectively. This gradation in weight allows taking an aliquot of the extract for analysis and having enough left over to challenge the next soil batch at the same liquid-to-solid ratio. Extracting 300 grams of waste yields sufficient solution to challenge three different kinds of soil in experiments set up with the proportions stated in Table 4.

Although the soil equilibrates in 6 hours or less (13), each solution was kept in contact with the batch of soil before filtration for the same length of time as used to extract the waste. This was to keep the samples progressing smoothly without gaps in the series. After filtering the soil extract, an aliquot was refiltered through Millipore and saved for analysis. The appropriate volume of the remaining filtrate was added to the next batch of soil. The soil exposed to the first waste extract was recovered and mixed with the second waste extract in the series. This was repeated until the waste had been extracted seven times and each waste extract had progressed through all three soil batches. (An eighth extract could have been made to further increase the equivalent leaching time.) This procedure was run in duplicate. When the volume of liquid became too large for the two-quart jar, the sample was transferred to a plastic five-gallon jug. (Square jugs with the opening above one side were the easiest to remove the contents from for filtering.)

Interpretation of Results

Plotting the waste output as in Figure 6 shows the depletion of the waste with continued leaching. To show the effect of passing the waste extract through soil, the histogram of Figure 11 is more useful. It presents the results obtained from extracting a batch of waste and using the solution to challenge a succession of three batches of soil. (Multiplying the observed concentration in micrograms/milliliter by the individual batch extraction volume per gram, milliliter/gram, converts the values to micrograms/gram of waste or soil. Micrograms per gram is equivalent to grams per metric ton of 1,000 kg or 2,205 lbs.) The height of the histogram bar labeled W represents the micrograms of. e.g., zinc extracted per gram of waste. This is the challenge to the batch representing soil section I. Because the liquid-to-soil ratio is kept the same for both the waste and the



11. Histogram showing the percentage and retention of a species by soil.

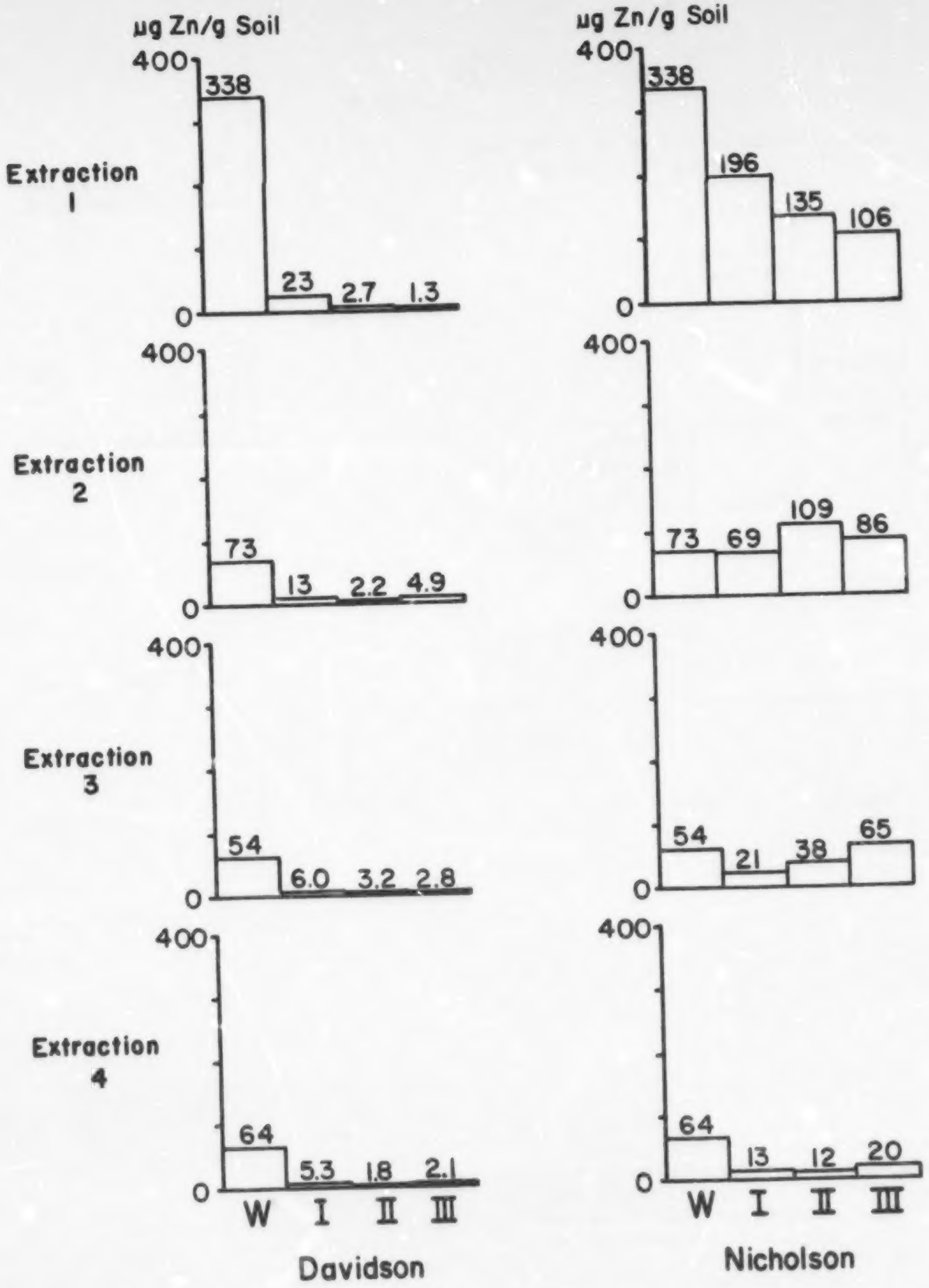
soil, W also is equal to the micrograms of zinc per gram of soil challenged. The height of the bar labelled I shows the concentration of zinc penetrating the batch representing soil section I, and the difference in height between I and W is the amount of zinc retained per gram of soil. The ratio of (W-I) to W is the fraction removed by that soil section. Similarly I is the challenge to II and bar II shows the penetration through II. If the fraction of zinc removed by each soil section is different, this shows that the removal characteristics of the soil are affected by conditioning and by changes in the extract. This can be further studied by comparing the histograms for the different extractions. When a histogram bar is higher than the preceding one, it shows that the soil is releasing zinc. The soil sections can be treated in pairs as above, or it can be considered that a given amount of waste has challenged three different amounts of soil: section I, section I + II, and sections I + II + III. Thus, the fraction removed can be calculated for three different waste-to-soil ratios.

The concentration, per gram soil, of a sorbed species divided by its concentration in the solution yields the distribution coefficient, which is the slope of the adsorption isotherm. By calculating a distribution ratio for each histogram bar, it is possible to follow the change in slope of the adsorption isotherm for each serial extraction (which show the effect of the changing sample matrix) and for *each different waste-to-soil ratio*. This is of considerable importance for modeling and for making predictions of contaminant movement through soils. (These relations will be developed in a later paper.)

Although several metal ions were found in significant concentrations in the battery waste leachate, zinc will be used here as the example. (The full discussion of all of the wastes studied will appear in a separate report.) Figure 12 presents a composite plot of histograms which show the extraction of zinc from battery waste and its penetration through Davidson and Nicholson soils. (Chalmers soil gave nearly the same results for zinc as did Davidson soil so is not plotted here.) Going vertically down the figure viewing any single column shows how the extraction of zinc and its retention by soil changes as the leaching progresses. For example, the W's show the depletion of zinc in the waste extracts, with an increase in the fourth batch probably due to the removal of other highly soluble species in the early extractions, resulting in an environment more favorable to the release of the remaining zinc.

It is seen that Davidson soil is considerably more effective in removing zinc from waste battery extract than is Nicholson soil. Although Nicholson soil has a much higher surface area and cation exchange capacity than Davidson soil the iron oxide content of the Davidson soil is much higher than the Nicholson. This is one of the factors influencing the difference in zinc removal by the two soils. The ability of Nicholson soil to remove zinc began to approach the removal capability of Davidson soil by the fourth in the series of extractions, either because of a conditioning of the Nicholson soil or because the zinc is then present in a waste leachate of different composition.

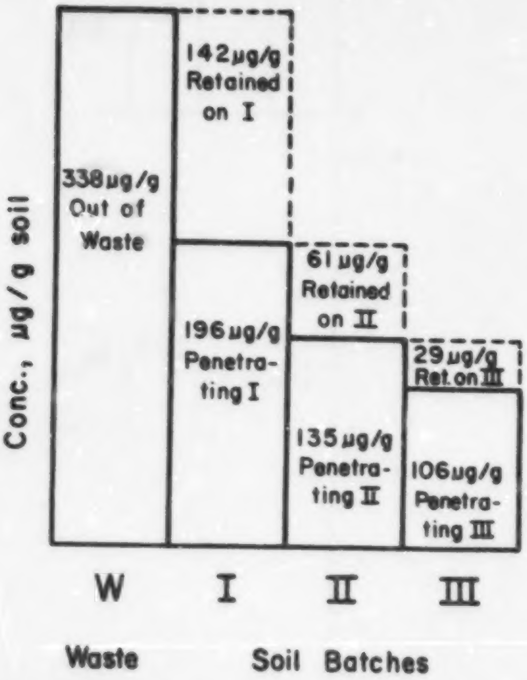
The Nicholson soil histograms for the second and succeeding extracts show a con-



12. The penetration of zinc in battery extract through soils.

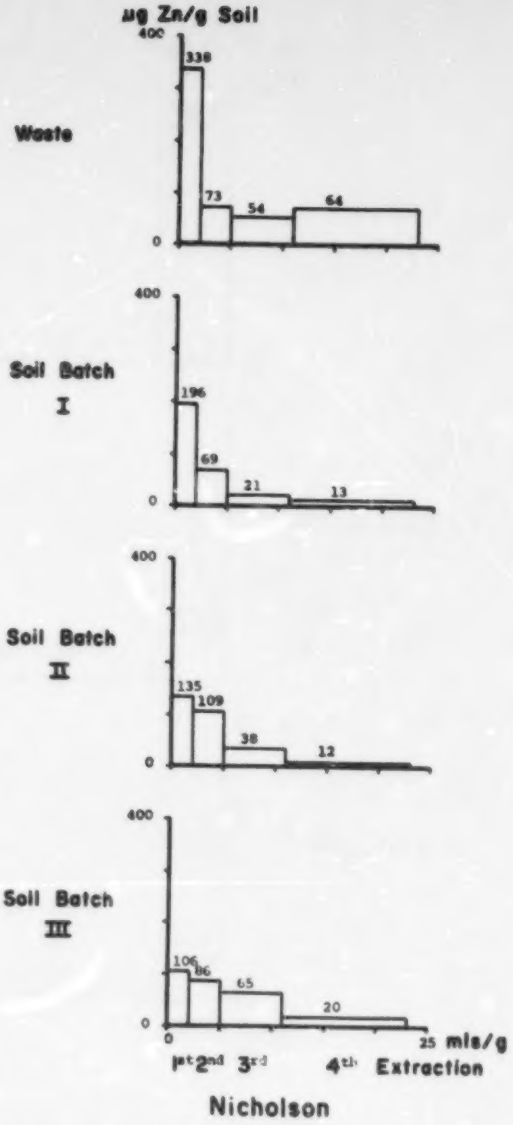
siderable release of zinc from the second or third soil batches. This is probably zinc taken out of previous extracts and later released by the soil due to the change in composition of the later extracts and the different soil history.

Each histogram of Figure 12 could have been treated as in Figure 13 by calculating the amount of zinc retained on the soil. This data can then be used to calculate the fraction of zinc removed from the extracts by the soil, or the fraction released from the soil as a peak elutes through the soil batches.



13. The penetration and retention of zinc in battery extract on Nicholson soil.

The method of Figure 6, which is particularly useful for graphing the waste extraction results, can be applied to the soils to emphasize the change in each succeeding extract. The widths of the histogram bars in this case represent the milliliters per gram used to extract each batch. The heights of the bars can denote the zinc concentration in µg/g, as depicted in Figure 14. If the bar heights stand for the observed zinc concentrations in µg/ml, the area under each bar is equal to the total number of micrograms of zinc extracted from that batch. (Concentration, µg/ml, times ml/g equals micrograms zinc extracted per gram of waste or soil.)



14. Plots emphasizing amounts extracted.

The conductance of every extract was measured to obtain an indication of the total concentration of ionized substances in the solution. The specific conductances graphed as column W of Figures 15 and 16 show that the soluble ions in the waste are rapidly leached out. When placed on batch

I of Nicholson and Davidson soils, the ions in the waste extract either penetrated the soils or they exchanged or displaced from the soil a comparable number of ions. The extracts from soil batch I produced roughly the same effect upon soil batch II. The conductance of the second waste extract was considerably lower than the conductance of the soil extracts, probably because residual soluble ions from the first waste extract were being washed through the soils. The ions appear to move as a broad peak in a manner similar to that obtained in elution chromatography.

The pH of the Nicholson soil extracts were considerably different from the Davidson soil extracts, as shown in Figures 15 and 16. Even though the first waste extract had a pH of 7.6, the Nicholson soil extracts from batches I, II, and III were quite acid: pH 5.8, 4.5, and 4.7, respectively, for the first extract. In comparison, the first Davidson soil extracts were 6.4, 6.3, and 6.4. The pH of the extracts from both soils were not comparable until they had been exposed to the fourth waste extract.

These batch testing experiments were also extended to determine the limiting soil capacity for the metals in the waste leachate. This work will be reported in a separate paper.

CONCLUSION

It has been demonstrated that the leaching of a waste by water or other solvent (e.g., the extract from another waste, such as municipal landfill) can be characterized and the ability of a soil to remove a chemical species from the waste leachate can be rapidly evaluated using serial batchwise extractions. The batch technique is also far more convenient than columns for rapidly investigating the effect of various environmental factors. Particularly if the extraction jars are sparged with nitrogen, this technique simulates the saturated anerobic conditions in the field. (This is considered the condition that would favor migration of cations through soil so the procedure may provide a "worst case" investigation into the suitability of the soil.) It is recognized that any effect of the waste leachate upon the soil's hydraulic properties can not be investigated using the batch method, but some columns can be set up to provide this data. (Hydraulic studies are quite simple to conduct because they use free-flow columns and do not require close monitoring or analysis of the soil leachate. Also, changes in the hydraulic properties caused by the waste leachate usually appear during the passage of the first few pore volumes of waste leachate.) Some columns can also be set up to follow long-term biological effects and similar slow changes.

No one method can give all the answers, but the graded serial batch approach can quickly provide much of the information needed to assess the categories of hazards from a class of wastes and to make decisions concerning the suitability of soil types for inhibiting the migration of hazardous chemicals.

ACKNOWLEDGEMENTS

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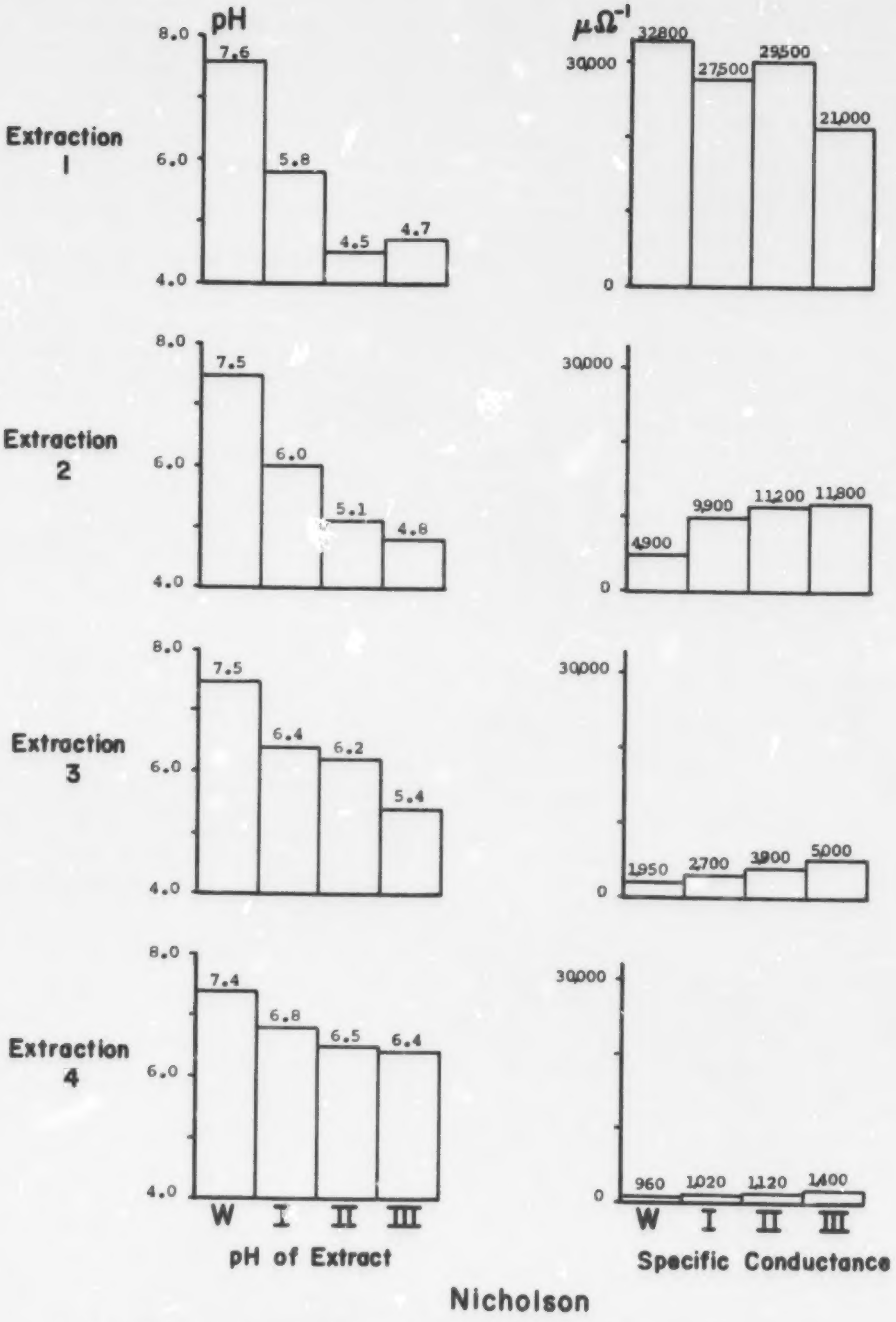
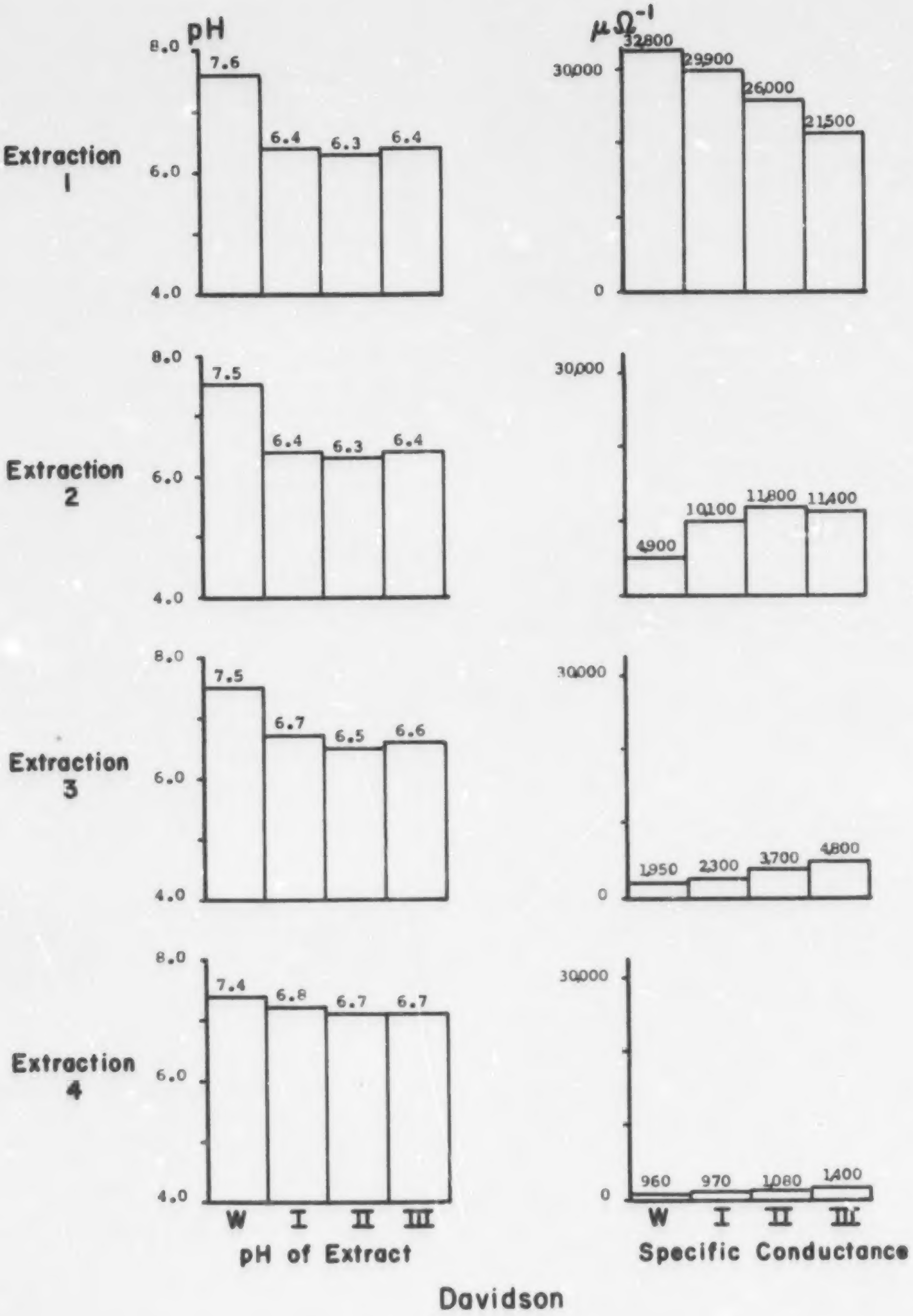


15. The pH and conductance of battery extract before and after passage through Nicholson soil.



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DISPOSAL AND REMOVAL OF POLYCHLORINATED BIPHENYLS IN SOIL

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ABSTRACT

The adsorption, mobility, and microbiological degradation of polychlorinated biphenyls (PCBs) in soil materials were studied relative to land disposal. The mobility of Aroclors 1242 and 1254 and a used capacitor fluid were measured by the soil thin layer chromatography technique. PCBs were immobile in all soils when leached with aqueous solvents (water and landfill leachate); they were highly mobile in all soil materials when leached with organic solvents.

The rate of adsorption of PCBs by soil materials was found to be rapid, with equilibrium conditions achieved in less than 8 hr. The adsorption process conformed to the Freundlich adsorption equation. PCBs were found to be strongly adsorbed by soil materials. The adsorption capacity and the mobility of PCBs were correlated to the organic carbon content and surface area of the respective soil materials.

Microbial degradation of PCBs was studied using mixed cultures of PCB-degrading microogranisms. Aerobic degradation of water-soluble Aroclor 1242 was 92 percent complete within 20 hr and as high as 98 percent within 10 days. PCB isomers with less than four chlorines were degraded while those with four or more chlorines were not significantly degraded. Soil samples collected from field plots where PCB-contaminated sewage sludge was applied for 7 years were found to contain mainly high chlorine substituted isomers. The field samples confirmed the mode of microbial degradation found in the laboratory studies.

INTRODUCTION

Polychlorinated biphenyls, or PCBs, have been manufactured since 1929. In the United States, they have been marketed under the trade name "Aroclor" by the Monsanto Company. It has been estimated that over 800 million pounds of PCBs have been produced. In 1970, the year of peak U.S. production, over 85 million pounds of PCBs were produced in the U.S. More than 57 percent of that amount was in the form of Aroclor 1242.(1)

The major application of PCBs has been in large electrical capacitors and transformers. PCB isomers having four or more chlorines per molecule are nonflammable and make excellent di-electric material for electrical equipment. Their unique properties led to many other applications such as hydraulic, vacuum-pump, and heat-transfer fluids. PCBs have been used as plasticizers, lubricants, inks, and pesticide extenders.(1)

Many of these uses led to the release of PCBs into the environment either accidentally or deliberately. Not until Jensen(2) reported PCB contamination of humans in 1966 was notice taken of PCBs in other environmental samples. In recent years, the accumulation of PCBs in humans and animal tissue and their toxic effects have been well documented.(3-5) PCBs have been identified as a significant hazard to human health as well as to the environment; their disposal has caused great concern.(6)

Incineration, considered the safest method of disposal of PCB wastes, is costly and can be a source of PCBs returning to the environment if operating conditions are not properly controlled.(7) Furthermore, since the major sources of waste PCBs are large electrical transformers and capacitors, the satisfactory incineration of the waste PCBs becomes even more complicated. Land burial, much less expensive and more energy efficient than incineration, is thus a more desirable alternative for disposing of PCBs. However, little information is presently available concerning the mechanism of attenuation of PCBs in soils or the possibility of groundwater contamination by PCBs leaching from landfills.

The water around a sanitary landfill was analyzed by Lidgett and Vodden,(8) who found no detectable (<4 ppb) PCBs in the water. Similarly, Robertson and Li(9) failed to detect PCBs in ground water using gas chromatography/mass spectrometry techniques. Moon et al.(7) reported that levels of PCBs in groundwater in the vicinity of eleven sanitary landfills were below detection (<1 ppb) but that low levels of PCBs were found in waters from monitoring wells at several industrial PCB disposal sites and lagoons. They concluded from analyses of water and split-spoon soil samples that PCBs are present in most leachates from land disposal sites and that PCBs have a strong affinity for soil. Tucker, Litschgi, and Mees(10) and Griffin et al.(11) also concluded that PCBs have a strong affinity for soil and that PCBs were not readily leached from soil by percolating water.

The above studies suggest that the interaction of PCBs with soil particles is an important attenuation mechanism. Another potentially important mechansim is the degradation of PCBs. Koeman(12) found that lower-chlorinated PCB isomers were found in animals low on the food chain, whereas higher-chlorinated isomers were found in animals high in the food chain. This seemed to indicate that the less-chlorinated isomers were less persistent, i.e. they were being degraded.

Many microorganisms have been reported that can degrade PCBs to some degree. Degradation has been demonstrated for a soil fungus, Rhizopus japonicua,(13) for a species of Nocardia, and for species of Pseudomon.(14,15) It has been known for some time that PCBs can be degraded by birds and mammals.(15,16)

PCBs frequently end up in sewers, either through spills or dumping. Herbst et al.(17) studied the fate of two radiolabeled isomers of PCB, a trichlorobiphenyl and a pentachlorobiphenyl, in an activated sludge unit. They found that the isomers were not degraded and that the major portion of the PCBs ended up in the activated sludge. However, Tucker et al.(18) reported that Aroclor 1242 was degraded by 26 percent in an activated sludge unit. Mihashi et al.(19) reported that PCBs were degraded by 50 percent in activated sludge and that the degree of degradation decreased as the chlorine substitution increased. PCBs have also been shown to be degraded by two species of Archromobacter(20,21) and by a Alkaligenes species(22) isolated from sewage.

The limited information presently available indicates that PCBs have a strong affinity for soil and are somewhat degradable by microorganisms. There is no evidence that ground water around sites containing relatively low levels of PCBs, such as sanitary landfills, has become contaminated with PCBs. However, surface and ground waters around some industrial disposal sites and around lagoons containing relatively large quantities of PCBs have become contaminated by leaching PCBs. The mechanisms of transport of PCBs in the biosphere and the mechanisms of attenuation in soil are unknown. Data on the factors affecting PCB attenuation by earth materials and the microbial degradation of PCBs would provide a useful basis for determining waste treatment methods, for predicting PCB migration under landfills, and for selecting and designing future disposal sites.

BACKGROUND

The research reported here is supported in part by Grant R-804684-01, from the U.S. Environmental Protection Agency, Muncipal Environmental Research Laboratory, Solid and Hazardous Waste Research Division, Cincinnati, OH 45268. Since the research is currently in progress, the techniques, results, and conclusions reported here should be considered as tentative and subject to revision and reinterpretation.

The purposes of the present project are: (a) to conduct an extensive literature review of pertinent information on the attenuation of PCBs in soil materials; (b) to measure the adsorption capacity of selected earth materials for pure PCBs and PCB wastes; (c) to quantitatively evaluate the effects of biological degradation, volatilization, time, and adsorbent structure on adsorption of PCBs; (d) to use this data to develop a mathematical model that will allow prediction of PCB adsorption and mobility; and (e) to further develop analytical procedures that will allow improved quantitative measurement of PCBs contained in aqueous solutions.

PCB Materials

Polychlorinated biphenyls (PCBs) is a generic term applied to certain mixtures of synthetic organic compounds. These compounds are mixtures of very closely related isomers and homologs that contain two phenyl rings with 10 possible chlorine attachments. The biphenyl structure is shown in Figure 1. PCBs are formed by substituting chlorine atoms for one or more of the hydrogen atoms at the numbered positions of the biphenyl structure. There are over 200 possible isomers; about 103 may occur in commercial PCB formulations.

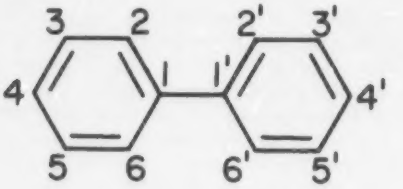


Fig. 1. BIPHENYL STRUCTURE: Positions 2 to 6 and 2' to 6' indicate ten possible positions for chlorine substitution. Different amounts of chlorine substitution form the various PCBs.

The PCB materials chosen for this study were Aroclor 1242 and Aroclor 1254 (42 and 54 percent chlorine, respectively). They were supplied by the Monsanto Company. The ^{14}C labeled compounds were prepared by New England Nuclear Corporation. Since gas chromatographic traces of the ^{14}C labeled compounds were identical to those of Aroclor 1242 and Aroclor 1254, respectively, it was assumed that there were no significant differences in the respective compounds and that the ^{14}C labeled and the Aroclors would behave similarly in studies of adsorption, mobility, and microbial degradation.

Also obtained for study was a used capacitor fluid drained from a burned out 50 KVA capacitor manufactured by Westinghouse in 1966 and originally containing Aroclor 1242. The capacitor fluid was analyzed for PCB with standard GC techniques and found to contain Aroclor 1242. However, the density of the capacitor fluid was measured to be 1.304 g/cc, while that for unused Aroclor 1242 was determined to be 1.354 g/cc. It is believed that the Aroclor 1242 in the capacitor fluid was less dense due to suspended carbon particles. These carbon particles gave the fluid a black color and are presumed to have been generated during the "burn out" of the capacitor. This capacitor was supplied by Illinois Power Company and was scheduled to be landfilled. We believe this fluid is representative of the type of PCB wastes that are normally disposed of in landfills.

Adsorbents

Earth materials, representing a wide range in characteristics, have been selected as adsorbents. The materials being studied are: Ottawa silica sand; Panther Creek southern bentonite clay; the soils, namely Bloomfield ls, Ava sic, Cisne sil, Flanagan sil, Catlin sil, Drummer sicl, Weir sic, a calcareous loam till; and two coal chars. The chars were selected because of their high adsorption capacity for organic compounds. Because they are a waste product of many coal conversion processes, they have potential use as a liner material for disposal sites accepting organic wastes.

Analytical Development

In general, PCBs are determined quantitatively by comparing gas chromatographic (GC) response patterns of a multicomponent environmental sample with commercial PCBs (Aroclor) or a mixture of Aroclors. This technique is limited by the sensitivity and reproducibility of comparisons of the large number of peaks produced by the various PCB isomers. The procedure is further complicated because the various components of water soluble PCBs contained in environmental samples are not likely to have the same composition as those in the original Aroclor used as a reference compound. For practical reasons, the quantitation is usually done by integration of the peaks and by comparison with standards of known isomeric composition. This can cause some error, depending on how well the mixture of isomers in an unknown sample compares to a standard.

Because of these problems, we have developed procedures that allow improved quantitative measurement of PCBs in aqueous samples. The main thrust of our studies has been to improve previous procedures whereby isomeric mixtures of PCBs were converted to the fully chlorinated biphenyl, decachlorobiphenyl (DCB), by digestion with $SbCl_5$. This procedure has the advantage of converting all the PCBs to a single peak for improved quantitation. The electron capture GC detector is many times more sensitive to DCB than it is to PCBs; thus, the conversion to DCB improves the sensitivity and lowers the detection limit for PCBs. Improved perchlorination procedures have been reported recently by Griffin et al.(11) and Berg et al.(23)

Further improvements in PCB analysis have been attempted during the project by experimenting with custom coatings of glass capillary columns for GC analysis. The liquid phase used was Emulphor ON-870, wall coated on 40 meter open tubular glass capillary columns. The procedures and apratus were based on the dynamic coating method of Grob.(24,25)

Generally, liquid phases for capillary gas chromatography can be divided into apolar, medium polar, and polar phases. Polar phase columns were notoriously short lived. Apolar liquid phases (OV-17, OV-101, SE-30, etc.) were widely accepted as the most efficient coatings due to their longer life; these generally are the ones available commercially. However, due to the aromatic characteristics of PCBs, a polar phase is needed to achieve maximum separation efficiency. The merit of the glass surface pretreatment methods given by Grob(24,25) is that polar phases such as Emulphor can be coated on the glass and used for PCB analysis with increased column life. In addition, the column can easily be regenerated. When a column has deteriorated to an unusable quality, a solution can be pulled through the column to wash out the residual liquid and the column can then be recoated. In the case of silicone liquid phases such as OV-17, OV-101, SE-30 etc., the regeneration step is not possible. Thus, capillary columns custom prepared for PCB analysis have superior separation efficiency compared to commercially available columns and have the advantage of being able to be regenerated.

CURRENT STUDIES OF PCB ATTENUATION

PCB Mobility: Determination by Soil Thin Layer Chromatography

The technique of determining pesticide mobility in soils by soil thin-layer chromatography was introduced in 1968 by Helling and Turner.(26) Since the introduction of the technique, the mobility of a large number of pesticides in a variety of soils has been tested.(27-29) Soil thin-layer chromatography, or soil TLC, is a laboratory method that uses soil as the adsorbent phase and a developing solvent (water, leachate, organic solvent, etc.) in a TLC system. The system is relatively simple and yields quantitative data on the mobility of organic compounds in soils that appear to correlate well with trends noted in the literature.(26) The results reported here are mobility data for Aroclor 1242 and Aroclor 1254 on TLC plates made from sand, three soils, and a coal char. Dicamba, a pesticide of known high mobility, was used as an internal standard.

The methods used to prepare soil TLC plates and to determine the mobility of PCBs in deionized water has been reported previously by Griffin et al.(11) In addition to using water as the developing solvent as reported previously, this paper reports the results of studies using landfill leachate and carbon tetrachloride as the developing solvent. The leachate was obtained from the Du Page County sanitary landfill (well MM63). The details of the site description and well location were given by Hughes et al.(30) Chemical characterization of the leachate was given by Griffin et al.(31) The three leaching solutions—deionized water, carbon tetrachloride, and leachate—were each extracted with hexane and analyzed for trace PCB using standard GC techniques and were found to be free from PCB.

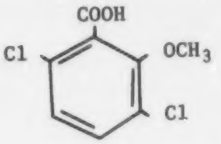
Generally, the mobility of PCBs was measured using radioactive ^{14}C labeled compounds as described by Griffin et al.(11) The resulting autoradiographs indicated the relative movement of the compound, which was measured as the frontal R_f of the spot or streak. The R_f value is defined as the ratio of the distance the compound moved relative to the distance the solvent moved. The R_f value is a quantitative indication of the front of PCB movement and a reproducible index of mobility.

To confirm the data obtained from autoradiographs and to obtain data for nonradioactive PCBs such as capacitor fluid, a zonal extraction technique was used. An individual lane of a plate was divided into 12 equal segments starting from 1.5 cm below the spotting origin of the particular compount and ending at 10.5 cm above the origin. The soil material from each segment on the plate was transferred to a glass centrifuge tube, and the PCBs were extracted into suitable organic solvents. In the case of radiolabeled compounds, the concentration of compound was determined with standard liquid scintillation techniques. With non-radiolabeled PCBs, the concentration in the extract was measured by GC techniques.

R_f values obtained from autoradiography were compared with those obtained by zonal extraction. The agreements were excellent. Autoradiography is especially satisfactory for soil TLC studies, as it provides a qualitative picture of movement (e.g. diffusion, tailing) while allowing measurement of frontal R_f. Zonal extraction gives a more quantitative picture of PCB movement. Also detected by the zonal extraction procedure are tailing, the origin spot, and the frontal movement of the compound. However, definition of the concentration profile is limited by the length of the soil segment chosen and by the extraction and analytical efficiencies. In summary, the two methods gave essentially identical pictures of PCB movement on TLC plates.

The mobilities of Aroclor 1242, Aroclor 1254, and Dicamba in several earth materials expressed as frontal R_f values are summarized in Table 1. The data for capacitor fluid are incomplete and are not shown in Table 1. However, all the results obtained to date are identical to those of Aroclor 1242 and will be discussed in that context. The data show that under the conditions tested, Aroclor 1242, Aroclor 1254, (and the capacitor fluid) stayed immobile in these soil materials when leached with water or Du Page leachate but were highly mobile when leached with carbon tetrachloride. Dicamba showed the reverse trend, being highly mobile in water and in Du Page leachate and quite stationary in carbon tetrachloride.

A closer look at the structure of Dicamba and PCB will help explain the mobilities observed. Dicamba is 3, 6-dichloro-o-anisic acid having the structural formula shown below:



With two polar groups—COOH and OCH_3, hydrogen bonding between the water molecules and the carboxyl and methoxy groups of Dicamba can occur and this increases the solubility of Dicamba in polar solvents. Solubility of Dicamba in water is 4,500 ppm.(32)

The PCB structure given in Figure 1 illustrates that PCBs are non-polar in nature and only very slightly soluble in polar solvents. Solubility of Aroclor 1242 in water has been determined to be 200 ppb.(10) and that of Aroclor 1254, 56 ppb.(33) However, PCBs are quite soluble in organic solvents such as C_6H_{14}, CCl_4, C_6H_6, CH_2Cl_2, and CH_3COCH_3. Mobilities of Aroclor 1242 and Aroclor 1254 were tested in silica gel leached with C_6H_6, C_6H_{14}, CH_2Cl_2, and CH_3COCH_3. Consistent with data from soil plates using CCl_4 as the developing solvent, R_f values of 1.00 were obtained for PCBs using these solvents on silica gel plates. It is obvious that mobilities of PCB and Dicamba in a given soil material are related to the solubility of PCB and Dicamba in the solvent with which the soil material is leached.

The above finding has great significance in PCB waste disposal. To prevent potential migration of PCBs in a land-

Table 1. Mobility of Aroclor 1242, Aroclor 1254, and Dicamba in several earth materials with various leaching solvents as measured by soil TLC.

	R_f Values								
	H_2O			DuPage Leachate			CCl_4		
	Aroclor 1242	Aroclor 1254	Dicamba	Aroclor 1242	Aroclor 1254	Dicamba	Aroclor 1242	Aroclor 1254	Dicamba
Ottawa silica sand	.03	.03	1.00	.03	.03	1.00	1.00	1.00	.02
Catlin Loam C_{ca}	.02	.02	1.00	.03	.03	1.00	1.00	1.00	.03
Ava silty clay loam B_2	.02	.02	1.00	.02	.02	1.00	1.00	.96	.02
Catlin silt loam Ap	.02	.02	.85	.04	.04	.90	1.00	1.00	.02
Coal char (1200°F)	.03	.03	.79	.04	.04	.80	1.00	1.00	.03

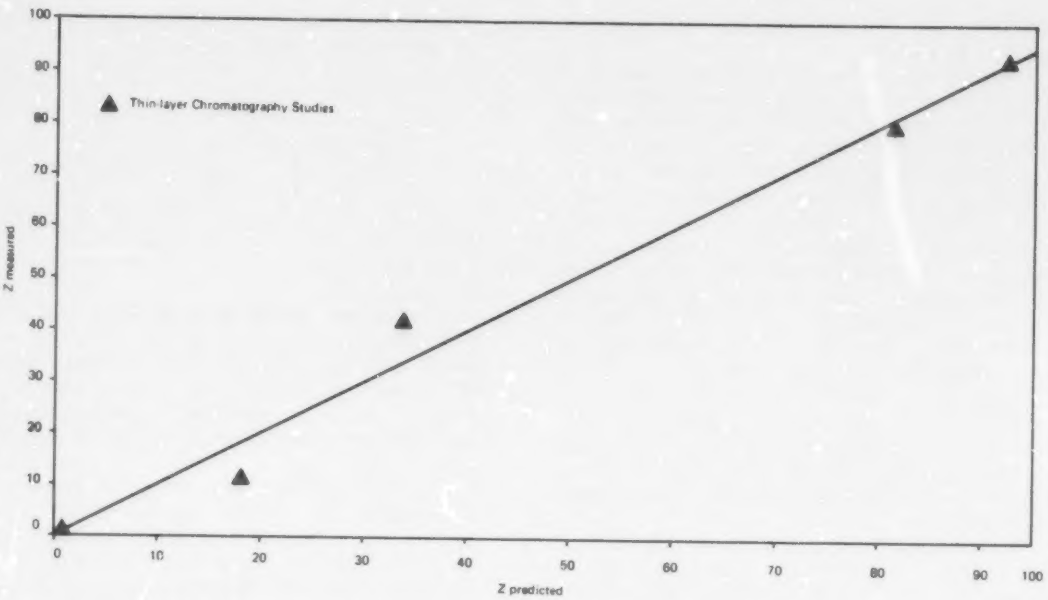


Fig. 2. Multiple linear regression of surface area and total organic carbon vs. adsorption of polychlorinated biphenyl (PCB) by several soils and coal char.

fill, PCB wastes and organic solvents should not be disposed of in the same landfill location,and the PCBs should not be allowed to come in contact with leaching organic solvents.

It is interesting to correlate the mobility of PCBs in CCl_4 with characteristics of the earth materials, e.g. clay content, surface area, pH, cation exchange capacity, organic matter, etc. The zonal extraction technique yields a quantitative measure of the quantity of PCB that moves to the top of each soil TLC plate with the solvent. Although PCBs have R_f values of 1.00 for all the soil materials leached with CCl_4 in Table 1, the percentage of PCBs that are retained against leaching are different for each of the soil materials. The mobility measured in this manner is correlated with the soil material properties.

Statistical methods were used to correlate soil material properties with the mobility of PCBs. Multiple linear regression analyses were performed on the data for surface area and total organic carbon of the soil materials vs. the mobility of PCBs. The following relation was obtained:

$$Z = -0.59 + 2.85x + 1.15y$$

where Z = the percentage of Aroclor 1242 retained against leaching by CCl_4 on soil TLC plates,

x = the surface area of the sample in m^2/g, and

y = the organic carbon content of the sample in percent.

A similar relation was found when data from the adsorption studies, to be reported in the following section, were evaluated. The results of a comparison between Z measured and Z predicted by this relation are presented in Figure 2. The excellent linear fit of the data to the theoretical line indicates that surface area and total organic carbon content are two major components of soil materials that can be evaluated to allow us to make predictions of PCB mobility in soils.

PCB Adsorption Studies

Equilibrium adsorption studies were carried out by shaking known volumes of PCB saturated water with varying weights of earth materials at a constant temperature of 25°C. The rate of adsorption of PCBs by earth materials was found to be rapid. Equilibrium conditions were achieved in less than 8 hr. The adsorption process conformed to the Freundlich adsorption equation:

$$x/m = K_F C^n$$

where x/m = the amount of PCB adsorption per unit weight (μg/g) of adsorbent (soil or char),

K_F = the Freundlich adsorption constant which is an indirect measure of the adsorption capacity of the adsorbent,

C = the equilibrium concentration ($\mu g/\ell$) of PCB in solution, and

n = a constant and the value of $1/n$ indicates the extent of adsorption.

The use of this relation allows quantitative predictions of PCB adsorption—by a given adsorbent—over the concentration range of water soluble PCBs.

The results of plotting the adsorption of water-soluble Aroclor 1242 by Ottawa sand (OS), montmorillonite clay (MC), Catlin soil (CS), high temperature char (HTC), and low temperature char (LTC) are shown in Figure 3, and the constants computed from the equation are given in Table 2. The value of r in Table 2 is the linear regression correlation coefficient for the data plotted in Figure 3.

PCBs were found to be strongly adsorbed by earth materials. Coal chars had the highest adsorption capacity, followed by

Table 2. Constants of the Freundlich isotherm equation

Adsorbent	$\frac{1}{n}$	n	K_F	r
Ottawa Sand	5.240	0.190	2.994×10^{-3}	0.731
Montmorillonite Clay	1.003	0.997	0.159	0.996
Catlin Soil	0.686	1.459	1.356	0.974
High Temp. Char	0.768	1.302	1.690	0.924
Low Temp. Char	0.567	1.764	7.486	0.972

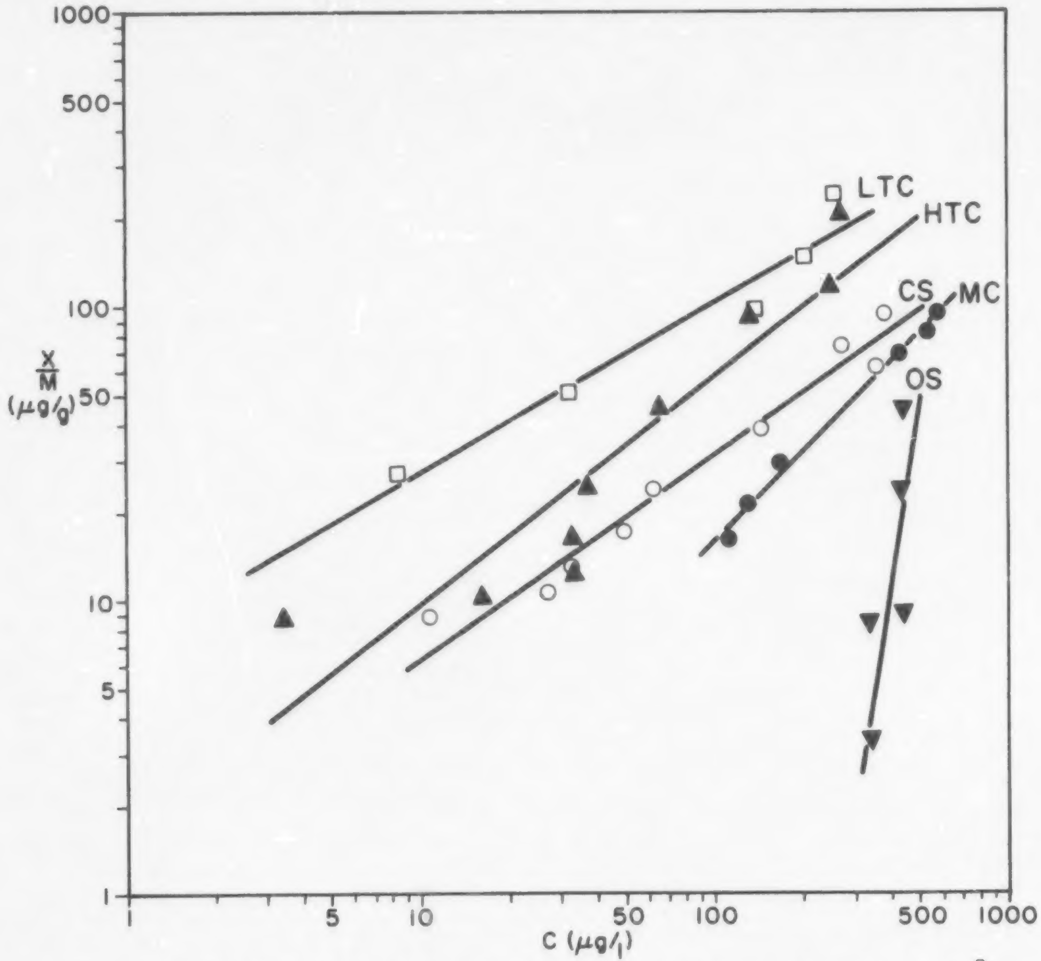


Fig. 3. Freundlich isotherm of Aroclor 1242 with different adsorbents at 25°C.

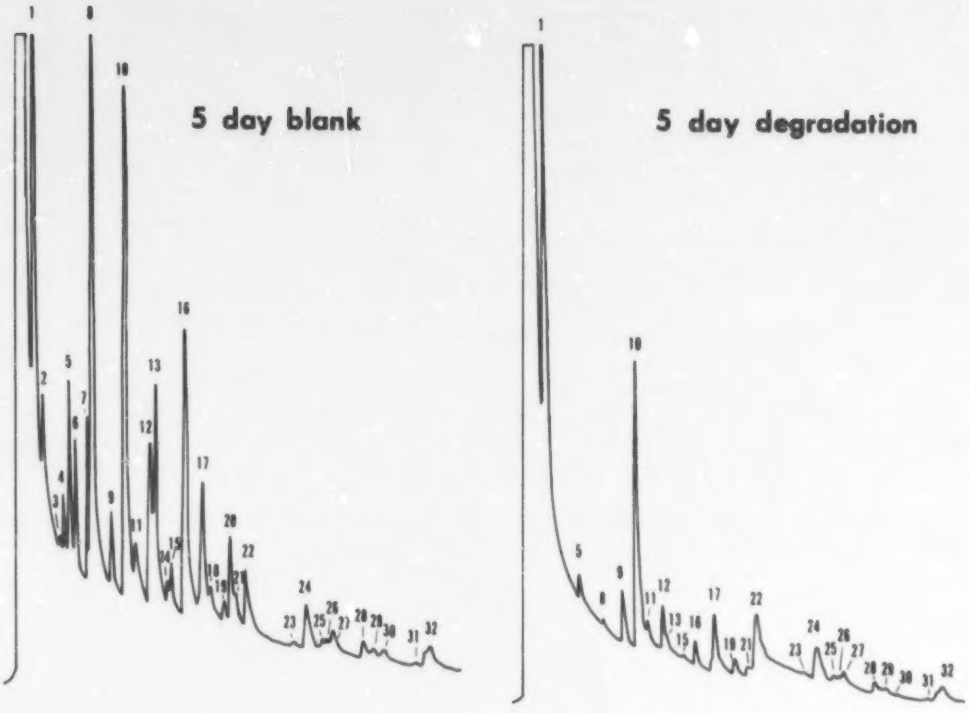


Fig. 4. Comparison of 5-day degradation and 5-day blank chromatograms.

soils, clays, and sand, which had progressively lower adsorption capacities. The adsorption capacity was found by multiple linear regression analysis to be correlated to the organic carbon content and surface area of the respective earth materials. Regression coefficients of 0.97 were obtained, indicating that these were the two major properties responsible for PCB adsorption.

Microbial Degradation of PCBs

Because PCBs appear to be somewhat degradable, attempts have been made in this study to select and enrich a mixed culture of soil bacteria that can significantly degrade PCBs. We feel that if the mixed culture, enriched in PCB-degrading organisms, can significantly degrade PCBs, then biological treatment units may be feasible to destroy waste PCBs or PCB wastes could be inoculated with the culture before land disposal. The microbial degradation, in conjunction with other means, can serve as an important mechanism for attenuating PCBs and preventing their movement into the biosphere.

Mixed cultures of PCB degrading microbes were isolated from soils and Hudson River sediments that had previously been contaminated with PCBs. Much greater activity of PCB-degrading microorganisms was found in the river sediment and in soils that had been previously exposed to PCBs than in soils that had no previous exposure. The presence of PCBs in a particular environment appears to enhance the selection of microorganisms capable of degrading PCBs.

In the study reported here, a mixed culture of microorganisms was isolated by biphenyl enrichment of soil from an experimental farm plot to which PCB contaminated activated sludge from a municipal waste treatment plant was applied for 7 years. We obtained several cores from both the treated plots and a nontreated plot to determine if PCBs were being degraded in the field.

Representative results of laboratory degradation studies using the sludge-treated-soil mixed culture and Aroclor 1242 are presented in Figure 4 and Table 3. Figure 4 shows both a chromatogram of a 5-day control and 5-day degradation;

Table 3: Microbial degradation of Aroclor 1242

Peak number	Number of chlorines	Percentage degradation After 20 hr.	After 5 days	After 10 days	After 15 days
2	1	100	100	100	100
3	1	100	100	100	100
4	2	74	100	100	100
5	2	51	93	99	99
6	2	100	100	100	100
7	2	98	100	100	100
8	2	99	99	99	99
9	3	84	88	89	89
10	3	49	67	70	71
11	3	81	90	90	89
12	2 + 3	65	71	76	78
13	3	87	99	99	99
14	3	100	100	100	100
15	3	93	98	100	100
16	3	75	96	98	98
17	4	46	72	75	76
18	4	99	99	99	99
19	4	54	72	76	73
20	3	99	100	100	100
21	4	69	~90	~90	~90
22	4	37	42	59	56
23	4	11	38	56	43
24	4	16	34	49	49
27	4	16	39	48	67
28	3	11	38	50	51
29	4	11	44	42	45
30	4	41	81	80	85
31	3	4	15	48	50
32	4	11	30	48	43
Total		92	97	98	98

many peaks are missing or reduced in the 5-day degradation sample.

Table 3 shows the amount of degradation of each peak when compared to the controls. The peak number refers to those peaks numbered in Figure 4. Peak 1 is an internal standard used for quantitation and is not a PCB. The number of chlorines refers to the chlorine content of a particular PCB isomer and was assigned to individual peaks using mass-spectrometer analysis. The standard deviation of the samples, expressed as percentage, ranged from 1 to 20 percent. Any degradation less than 50 percent was considered insignificant.

The data presented in Table 3 show that all of the monochloro-isomers and most of the dichloro-isomers were degraded in less than 5 days. Many of the trichloro-isomers were largely degraded, whereas only a few of the tetrachloro peaks show these isomers to have undergone significant degradation.

Because much of the degradation occurred in less than 5 days, samples were subsequently run for 20 hours to determine which peaks were most easily degraded. The results can be compared to the results for 5-, 10-, and 15-day degradation (table 3). Both of the major monochlor-isomers are degraded in 20 hours; however, dichloro peaks 4 and 5 are still present to some degree. Many of the trichloro-peaks showed much less degradation in 20 hours than in 5 days. The tetrachloro peaks showed much less degradation in 20 hours as compared to the longer degradation times.

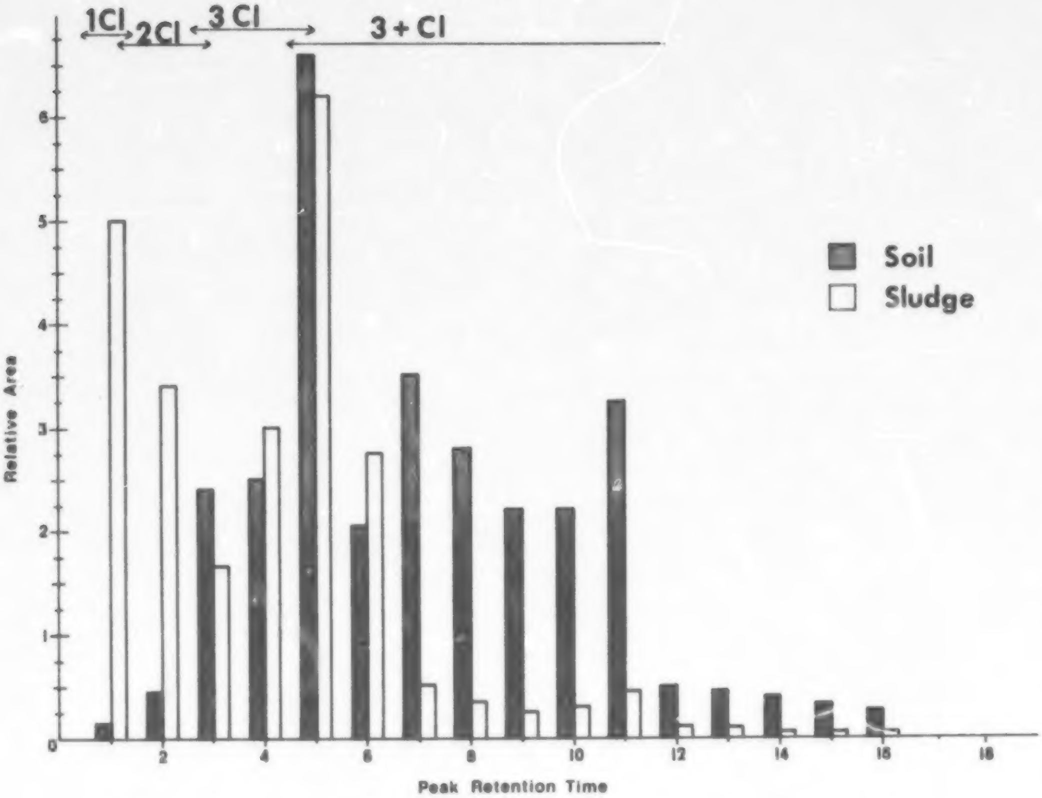


Fig. 5. Relative distribution of peaks in soil and sludge extracts.

These results are consistent with previous evidence that the lower-chlorinated isomers of PCBs are more easily degraded than the higher-chlorinated isomers.(14-16, 18, 20-22)

These results also were in accord with the preliminary data obtained from the soil and sludge extract experiments. Comparison of the chromatograms of the soil and sludge extracts with a chromatogram of Aroclor 1242 and Aroclor 1254 illustrated which peaks were PCBs and which were other compounds. Degradation of PCBs in the sludge-treated soil could be determined by comparing the gas chromatogram of the soil extract with that of the sludge extract. Figure 5 shows the results of the soil extract compared to those of the sludge extract. The sludge has predominantly low-chlorine isomers (low retention time), whereas the soil contains predominantly high-chlorine isomers (longer retention time). This indicates that the lower-chlorinated isomers that were placed in the soil from the sludge have been degraded, while the higher-chlorinated isomers, which are more slowly degraded, have apparently accumulated in the soil.

Because the results of the soil extraction study are preliminary, we are not able to estimate quantitatively the amount of degradation or accumulation in this soil. Only traces of PCBs were detected at depths of 6 to 12 inches in the soil profile, and no PCBs were detected at depths greater than 12 inches, even though PCB-contaminated sludge had been applied to this plot for 7 years. PCBs, therefore, appear to be highly immobile in this soil. The conclusion is consistent with the findings of the mobility and adsorption studies reported above.

Several points must be clarified when interpreting the results of this study. First, a mixed culture of microorganisms was used that contains at least four distinct types of microbes. This is in contrast to the pure cultures of PCB-degrading microbes used by most other researchers. Therefore, the degradation of the PCBs found in this study, more rapid than previously reported degradation, can be attributed partly to the use of the mixed culture. For example, in addition to the PCB-degrading microbes, such a culture may have other species of microorganisms that can degrade the PCB metabolites produced by the PCB-degrading microbes. The degradation of the metabolites thus leads the way for further degradation of the PCBs by removing potentially inhibitory products. This mixed culture approach is closer to the conditions that exist in the environment than is a pure culture system.

Second, only water-soluble PCBs were used. Water-soluble and total PCB have different relative proportions of PCB isomers.(33,34) Therefore, 90 percent degradation of water-soluble PCBs is less than would be achieved for total PCBs. However, since most potential migration of PCBs would occur in an aqueous environment, the degradation of the water-soluble isomers are clearly the more environmentally significant.

Since the mixed culture was enriched from soil to which PCB-containing sludge had been applied, and since it appears that there were already PCB-degrading microbes present, PCBs should be degraded to some extent in the environment. This was indeed found with the soil extracts in this study. Koeman(12) pointed out that most PCB residuals in animals yield GC chromatograms similar to Aroclor 1260, a rather highly chlorinated series of PCB isomers. Other researchers(35) have reported a predominance of the higher-chlorinated isomers in environmental samples. Because Aroclor 1242, a relatively lower-chlorinated series of isomers, accounted for the majority of PCBs produced and marketed, it would appear that the lower-chlorinated isomers are degraded in the environment, at least to some extent. The isolation of microorganisms from soil that can degrade PCBs readily suggests the possibility of future inoculation of wastes containing PCB before disposal or biological digestion prior to disposal.

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Land Disposal of Hexachlorobenzene Wastes:

Controlling Vapor Movement in Soils

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ABSTRACT

The disposal/storage of potentially volatile hazardous waste on land suggests the need for developing information on controlling vapor movement in soils. This information would be useful for the purpose of limiting vapor phase transport through a soil cover to the surrounding atmosphere to an acceptable level. Hexachlorobenzene-containing industrial waste (hex waste) was used as the source of a volatile compound in a laboratory study of the important soil parameters controlling vapor movement. Volatilization flux through a soil cover was directly related to soil air-filled porosity and was greatly reduced by increased soil compaction and increased soil water content. This paper reports on the application of these research findings in developing predictive equations for use in designing landfill covers.

The soil has proven to have tremendous capacity for neutralizing certain of the wastes produced by society. When properly managed this waste-handling capability can be utilized to the fullest. Likewise when mismanaged the consequences can be severe, expensive and long-term. One of the management tools required for the utilization of land as a waste disposal medium is the ability to control volatilization of wastes in landfill. This project was designed to gather laboratory data useful to the landfill planner in controlling vapor movement through the soil cover of a landfill. The study was carried out using hexachlorobenzene (HCB) from HCB-containing industrial wastes as a model for the volatilizing compound.

Hexachlorobenzene is present in industrial wastes as a by-product of certain commercial production processes. A recent EPA report(1) indicated over 3900 metric tons (8.5 million pounds) of HCB produced annually. This HCB is contained in over 24,000 metric tons (53 million pounds) of industrial waste, a significant amount of which is disposed of on landfill. Other methods currently being used for disposal of HCB-containing wastes (hex waste) range from temporary storage in water covered lagoons to more permanent storage via deep well injection. Successful incineration in highly efficient devices has been demonstrated and is in use. The major source of hex waste (ca. 90%) is as a by-product in the commercial production of several chlorinated solvents such as perchloroethylene and carbon tetrachloride. In addition significant quantities of HCB are produced as impurities or by-products in the production of chlorine gas and in the production of certain pesticides.

HCB appears to be widespread in the environment. Residues have been found in soil, wildlife, fish and food samples as well as in humans.(2,3,4) The source of this HCB is not always known as the residues are reported across the United States as well as around the world. Widespread contamination of cattle, soil, plant and humans was discovered in Southern Louisiana in 1973 near HCB production facilities and municipal landfill facilities which accepted hex waste.

In past Symposia(5,6) we have reported on a number of aspects of land disposal of hexachlorobenzene wastes. These included a statement of the problem, properties of HCB, and experimental results dealing with transport of HCB in soil especially vapor transport. Following a brief review of earlier reports, this Symposia will report on the application of research results to designing a landfill cover for reducing HCB volatilization.

Hexachlorobenzene is a persistant, water-insoluble, fat-soluble, organic compound. Because of its low water solubility (6.2 ug/l), transport in moving water will be negligible. Its long term persistance and appreciable vapor pressure (1.91×10^{-5} mm Hg at 25 C) allows significant volatilization to occur. The potential for volatilization indicates a need for disposal site coverings that will reduce the vapor phase transport of HCB into the surrounding atmosphere.

Experimental procedures were developed and evaluated in our laboratory using a simulated landfill to determine the parameters necessary to predict HCB volatilization from hex waste placed under a soil cover. These procedures and results have been detailed in a previous symposium.(6) Briefly it was found that soil depth and soil air-filled porosity were the two prime factors controlling vapor movement in soil. This relationship between soil depth, soil air-filled porosity, and vapor flux is a direct result of the nature of vapor phase diffusion in soil. Since HCB is essentially insoluble in water, diffusion in soil pores will be the only mechanism available to HCB molecules for movement. Furthermore, because of the much greater quantity of HCB in the vapor phase compared to that in solution, HCB diffusion will be primarily in the vapor phase. This leaves us with a diffusion controlled process involving only air-filled pores. This will be the process controlling movement of HCB molecules to the soil surface of a landfill cover. Once the HCB molecules reach the soil surface they will be carried rapidly away by air currents.

The volatilization or vapor loss of HCB and other compounds from landfill can be treated as a diffusion controlled process. The rate at which compounds will volatilize from the soil surface and be lost to the atmosphere will be controlled by the rate at which they diffuse through the soil cover over the waste. Assuming no degradation of the compound and no transport in moving water, the volatilization can be predicted using Fick's First Law for steady state diffusion:

$$J = -D_s(C_2 - C_s)/L \qquad (1)$$

where J is the vapor flux from the soil surface (ng/cm^2/day),

D_s is the apparent steady state diffusion coefficient (cm^2/day),

C_2 is the concentration of the volatilizing material in air or vapor density at the surface of the soil (ug/l),

C_s is the concentration of the volatilizing material in air or vapor density at the bottom of the soil layer (ug/l), and

L is the soil depth.

The negative sign is present to indicate that the vapor flux is in the opposite direction from the vapor concentration gradient in the soil. Table 1 gives several conversion factors which may be useful depending on whether regulatory agencies specify flux in metric or English units.

Table 1. Conversion Factors

To convert	into	multiply by
atmospheres	mm Hg	760
centimeters	ft	3.28×10^{-2}
cm^2/day	mm^2/week	700
feet	cm	30.48
g/cm^3	lbs/ft^3	62.4
kg/ha	lbs/acre	0.89
mm Hg	atm	1.32×10^{-3}
ng/cm^2	kg/ha	10^{-4}
ng/cm^2	lbs/acre	8.9×10^{-5}

In order to use Equation (1) for predicting volatilization, the apparent diffusion coefficient, D_s, must be evaluated. The investigators, Millington and Quirk (7) have suggested an apparent diffusion coefficient which included a porosity term to account for the geometric effects of soil on diffusion.

$$D_s = D_o(P_a^{10/3}/P_T^{\,2}) \qquad (2)$$

where D_o is the vapor diffusion coefficient in air (cm^2/day),
P_a is the soil air-filled porosity (cm^3/cm^3), and
P_T is the total soil porosity.

Combining Equations (1) and (2) yields the following expression:

$$J = -D_o(P_a^{10/3}/P_T^{\,2})(C_2 - C_s)/L \qquad (3)$$

This equation will be used in this paper as the basis for a suggested step-wise procedure intended to assist a planner in designing a landfill cover that minimizes the escape of HCB or other vapors. Alternatively, an existing landfill cover may be assessed, using Equation (3), for its potential for allowing HCB vapor flux through the surface of the landfill. The validity of Equation (3) has been experimentally verified for hexachlorobenzene in our laboratory using a simulated landfill and HCB-containing industrial waste as the volatilizing compound.(7) The diffusion coefficient in air, D_o, for HCB was found to be 1×10^4 cm^2/day.

This procedure for assisting in the design of a landfill cover is only a suggested procedure and is not an accepted official EPA procedure. This will be an example of how research findings can be used to arrive at a suggested set of procedures that will assist planners in designing landfill covers taking advantage of the best current knowledge available for reducing vapor flux from a landfill.

DESIGN APPLICATION

In order to use the results of this study in designing a proposed landfill, the planner will normally begin with an acceptable value for HCB flux through a cover and determine the most efficient combination of soil porosity and soil depth to produce the acceptable value. The establishment of the actual values for an acceptable flux thru the landfill cover is beyond the scope of this research or that of the landfill designer. Flux from the soil will be established through regulations by state or federal agencies. Alternatively the regulating agencies may establish acceptable air concentration values at some specified distance from the landfill site. In the latter case the landfill designer may have to calculate the acceptable flux at the soil surface using the specified air concentration and existing wind dispersion models.(8)

Once an acceptable flux value has been established either directly by a regulatory agency or indirectly by use of an air dispersion model, the following steps can be followed to determine what soil conditions would limit flux to this value. The following steps are based on Equation (3) relating vapor flux through soil to soil depth and soil porosity. Initially the soil depth necessary to produce the desired flux will be calculated assuming a dry soil and a minimum reasonable compaction of the soil at the landfill site. If this calculated soil depth is unrealistically high, then increased compaction and/or an appropriate water content will be considered. Finally a modified soil will be considered when necessary and a new flux value calculated. Equation (3) is rearranged below to allow calculation of L, the soil depth (cm).

$$L = -D_o (P_a^{10/3}/P_T^{2})(C_2 - C_s)/J$$

or

$$L = -D_o P_a^{10/3} (C_2 - C_s)/JP_T^{2} \qquad (4)$$

By assuming that C_2 is zero, Equation (4) simplifies as follows:

$$L = D_o C_s P_a^{10/3}/JP_T^{2} \qquad (5)$$

This is a reasonable assumption since under actual landfill conditions the amount of vapor reaching the soil surface from below hopefully will be small and will be rapidly dispersed by wind currents and by diffusion in air. Additionally the assumption of C_2 equaling zero introduces a safety factor into the calculation. Any increase in C_2 will reduce the vapor flux from the soil surface.

The diffusion coefficient in air for HCB has been measured to be 1.0×10^4 cm^2/day. If soil cover is being designed for some material other than HCB, values for diffusion coefficients in air are available for a limited number of compounds.(9) For those compounds of interest for which no published values are available, reasonable estimates can be made using the following. The vapor diffusion coefficient of compound A can be estimated from the known vapor diffusion coefficient of compound B by using the following equation:

$$D_A = D_B (M_B/M_A)^{\frac{1}{2}} \qquad (6)$$

where the subscripts A and B denote the values of the diffusion coefficients for compounds with molecular weights M_A and M_B, respectively.

When the temperature changes from T_1 to T_2, where T is the absolute temperature (°K), the diffusion coefficient at temperature T_2 can be estimated using the following equation:

$$D_2 = D_1 (T_2/T_1)^{\frac{1}{2}} \qquad (7)$$

where the subscripts 1 and 2 denote the values of the diffusion coefficients at the temperatures T_1 and T_2, respectively.

The value for the vapor concentration at the bottom of the soil layer, C_s, can be taken as that equivalent to the saturation vapor pressure of the pure compound. This is true because a waste need contain only a relatively small amount of a volatile material to give a saturated vapor. In the case of HCB, a saturated vapor density was obtained with only 2% HCB coated on sand. It is conservative to assume C_s equal to the saturation vapor pressure. If the actual vapor pressure is less than saturation, the actual vapor flux through the surface of the soil layer will be less than calculated. Saturation vapor densities are calculated from the following using vapor presure data which are available for a number of compounds.(9,10)

$$C_s = pM/RT \qquad (8)$$

where p is the vapor pressure (mm Hg),
M is the molecular weight of the compound (ug/mole),
R is the molar gas constant (1 mm Hg/deg mole), and
T is the absolute temperature (°K).

The value of C_s for HCB is 0.294 ug/l at 25 C calculated from a vapor pressure of 1.91×10^{-5} mm Hg.

Based on the above considerations the following steps are to be followed in calculating the optimum combination of soil depth and soil porosity to achieve the desired vapor flux. A suggested method or sequence for working through these steps is shown in Figure 1.

1. Base all flux calculations on total soil porosity assuming a dry soil. Thus $P_a = P_T$ and Equation (5) is further simplified to

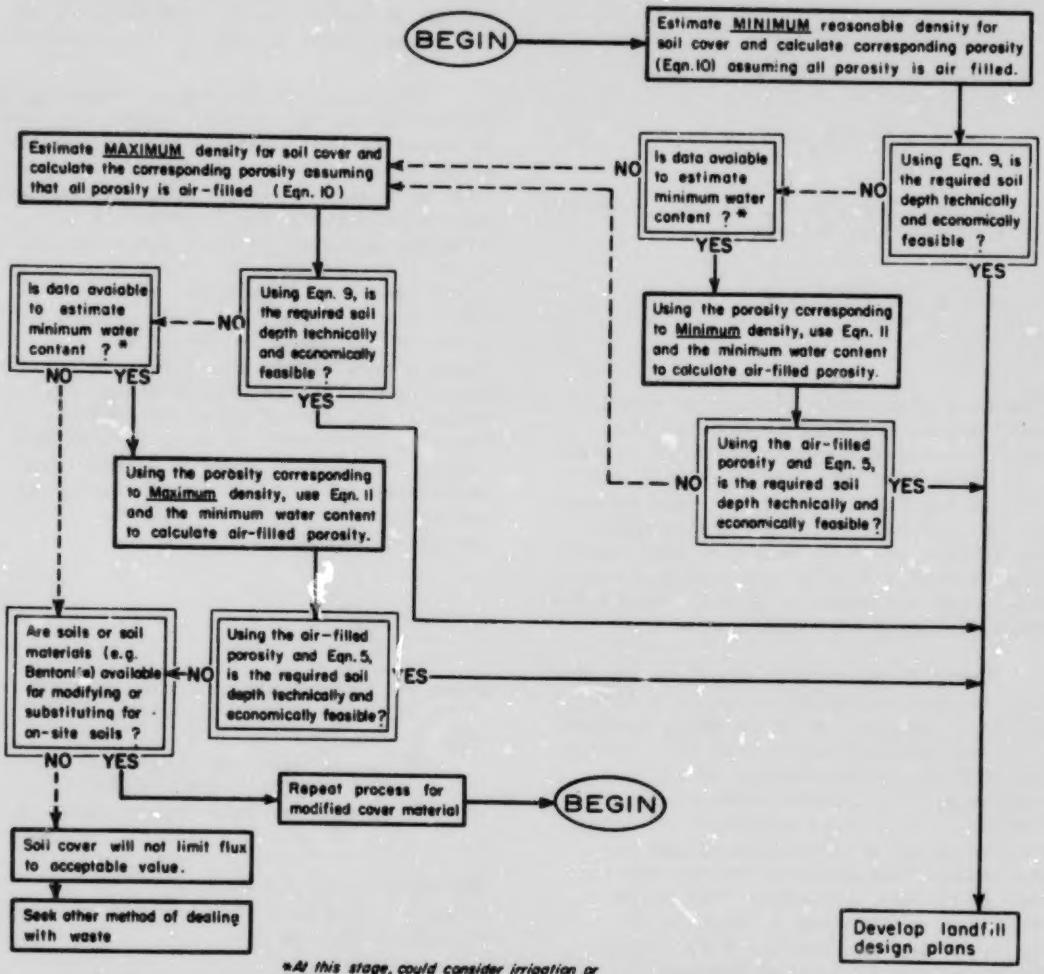
$$L = D_o C_s P_T^{4/3}/J \qquad (9)$$

This not only simplifies the calculations but introduces another safety margin.

The addition of any water to the soil by irrigation or by natural rainfall will reduce the air-filled porosity and thereby reduce the vapor flux from the soil surface. The total porosity of the soil can be calculated from the soil bulk density, β, using the following equation:

$$P_T = 1 - \beta/\rho \qquad (10)$$

where β = soil bulk density (g/cm^3) and
ρ = particle density (g/cm^3).


BEGIN
Estimate MINIMUM reasonable density for soil cover and calculate corresponding porosity (Eqn.10) assuming all porosity is air filled.
Using Eqn. 9, is the required soil depth technically and economically feasible ?
NO
YES
Is data avaiable to estimate minimum water content ? *
NO
YES
Estimate MAXIMUM density for soil cover and calculate the corresponding porosity assuming that all porosity is air-filled (Eqn. 10)
Using the porosity corresponding to Minimum density, use Eqn. 11 and the minimum water content to calculate air-filled porosity.
Using the air-filled porosity and Eqn. 5, is the required soil depth technically and economically feasible?
NO
YES
Using Eqn. 9, is the required soil depth technically and economically feasible ?
NO
YES
Is data avaiable to estimate minimum water content ? *
NO
YES
Using the porosity corresponding to Maximum density, use Eqn. 11 and the minimum water content to calculate air-filled porosity.
Using the air-filled porosity and Eqn. 5, is the required soil depth technically and economically feasible?
NO
YES
Are soils or soil materials (e.g. Bentonite) available for modifying or substituting for on-site soils ?
NO
YES
Repeat process for modified cover material
BEGIN
Soil cover will not limit flux to acceptable value.
Seek other method of dealing with waste
Develop landfill design plans

*At this stage, could consider irrigation or other treatment to maintain higher water content (if allowed by regulatory agency)

Figure 1. Flow diagram for predicting depth of soil cover required to limit vapor flux through soil cover to an acceptable value.

The particle density can be measured. However, the particle density for most soil mineral material is usually taken as 2.65 g/cm^3 (165 lbs/cu. ft.).

2. Establish a minimum and maximum soil porosity that is likely to be achieved through maximum and minimum compaction of the soil type available at the proposed landfill site. Standardized procedures such as the Procter (ASTM D-698) (11) and modified Procter (ASTM D-1557) (11) tests are available for estimating the densities that can be achieved for a given soil with various degrees of effort. The degree of compaction need not be limited to either minimum or maximum as intermediate values may be calculated if necessary to determine the precise limiting density.

3. Using the porosity value established in Step 2 above, Equation (9) is used to determine the depth of soil necessary to attain the acceptable vapor flux value through the soil surface.

4. If circumstances allow an estimate of long-term soil water contents in the landfill cover, the planner can refine the flux calculations to give a reduced flux due to reduced air-filled porosity. This refinement requires the use of Equation (5), taking into account the air-filled porosity as affected by soil water content. The air-filled porosity, P_a, is calculated from the total porosity, P_T, and the volumetric soil water content, θ, by the following:

$$P_a = P_T - \theta \qquad (11)$$

The volumetric water content (cm^3/cm^3) is determined from the gravimetric soil water content as follows:

$$\theta = W\beta / \rho_w \qquad (12)$$

where W is the gravimetric soil water content (g/g), and ρ_w is the density of water (g/cm^3). For practical purposes the density of water can be taken as one and the volumetric water content is simply the gravimetric water content multiplied by the soil bulk density, β.

5. If the soil depths calculated in the previous steps prove to be too great to be technically or economically feasible then the planner will need to decide if it is possible to replace or modify the on-site soil with other soil materials (e.g., bentonite) to increase soil bulk density. If soil modification is feasible than it will be necessary to go back and calculate a new soil porosity term, and thus a new flux value, using the higher bulk density.

6. If none of the above procedures will produce a soil cover that will limit the vapor flux to an acceptable value, other disposal methods may have to be considered for dealing with the waste.

ASSESSMENT APPLICATION

In the case where an existing landfill site has a history of accepting and disposing of HCB-containing materials or other waste of similar concern, it may be desirable to evaluate the cover and to estimate the HCB vapor flux through the surface of the soil to determine if the landfill cover should be redesigned.

Equation (9) is rearranged as follows to calculate vapor flux through a dry soil cover of depth, L, and total porosity, P_T.

$$J = D_o C_s P_T^{4/3} / L \qquad (13)$$

The same considerations apply to the use of this equation for calculating flux as applied to Equation (9) for calculating soil depth:

1. The diffusion coefficient in air for HCB is 1.0×10^4 cm^2/day. For other compounds, a value for D_o can be estimated if the actual value has not been determined.

2. The concentration in air at the soil surface, C_2, is assumed to be zero. As discussed before, this is a reasonable assumption and introduces a safety factor into the calculation of a maximum value for the vapor flux through the soil surface.

3. The concentration in air at the bottom of the soil layer. C_s, is the saturation vapor concentration of the compound calculated from its vapor pressure data.

4. In making these calculations a dry soil is assumed so that $P_a = P_T$.

5. If data is available on soil water content, Equation (5) can be used to estimate vapor flux.

DISCUSSION

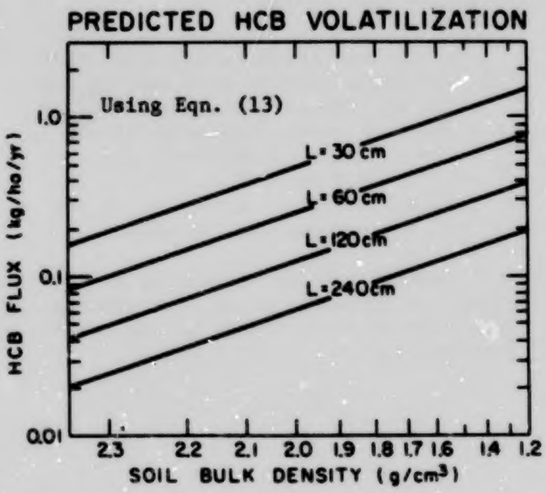


Figure 2. Predicted hexachlorobenzene volatilization fluxes through a soil cover of various soil bulk densities and soil thicknesses. The soil is assumed to be dry in order to yield a maximum vapor flux through the soil cover.

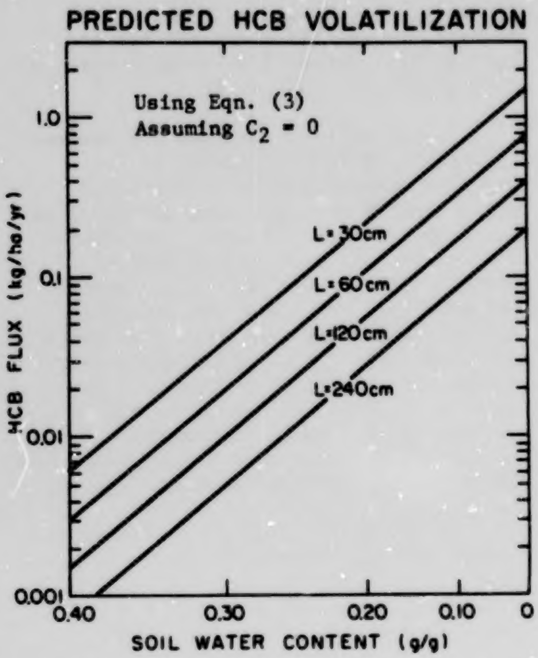


Figure 3. Predicted hexachlorobenzene volatilization fluxes through a soil cover of various soil water contents and soil thicknesses. Soil bulk density is 1.2 g/cm^3 (74.9 lbs/cu ft).

Figures 2 and 3 illustrate the use of Equation (13) for predicting vapor flux at different depths of soil cover. Figure 2 shows the HCB volatilization fluxes through soil cover with dry soil at various bulk densities and thicknesses. Soil temperature was taken as 25 C. The vapor fluxes shown in Figure 2 are the maximum to be expected through the soil cover because the addition of water would reduce the air-filled porosity and thus reduce the vapor flux through the soil. Figure 3 shows the predicted HCB vapor flux through a soil cover at various soil water contents and soil depths with the soil bulk density held constant at 1.2 g/cm^3 (74.9 lbs/cu. ft.).

These procedures are written for application to disposal of HCB-containing wastes. However, these same methods can be used to aid in designing landfill covers for other compounds as well, subject to the following qualifications. Hexachlorobenzene degrades very slowly, if at all. Since HCB is very slightly soluble (6.2 ug/l) its transport by moving water is negligible. For compounds which degrade more readily or are more mobile in moving water than HCB, these procedures will tend to overestimate the actual flux through the soil cover. These procedures assume no movement of the compound in water which may be percolating through the soil profile. If a compound is more soluble in water than HCB, it may eventually move with the water its actual mobility being dependent upon the extent it is adsorbed by the soil materials. Assuming that net water flow will be downward in soil, mobility in water will move the compound away from the surface of the soil cover. These procedures assume no decomposition of the material. Any decomposition which may occur will serve as a sink for the compound and will decrease the amount escaping as a vapor. The procedures presented here, therefore, will not account for any reduction in vapor flux due to decomposition of the compound or due to transport of the compound in water.

If hex wastes are to be placed on land, our work has shown the importance of minimizing the air-filled porosity of soil covers. However, our contribution to the design of a landfill assumes an intact soil cover is maintained. If any cracks or other small openings develop in the soil cover, they will result in an appreciable increase in HCB flux through the soil cover. The placement of hex waste with any material, such as municipal solid waste, that are subject to settlement could cause such cracking and flux increase.

If hex wastes are placed on land, consideration should be given to the need for long-term arrangements for ensuring the integrity of soil covers. Calculations assuming no degradation indicate that HCB placed on land could continue to volatilize at a maximum rate for several centuries. The integrity of the soil cover must be maintained for this period by preventing such things as erosion or digging.

In addition to soil as a cover, we have examined the efficiency of water and polyethylene film as covers for reducing vapor movement of HCB. Both water and polyethylene film have been used in actual disposal of hex waste. Water lagoons have been used for the temporary storage of hex waste and polyethylene films have been used in conjunction with a soil cover. In our studies water was highly effective in reducing volatilization of HCB. Polyethylene film was about as effective as water. However, the cost of polyethylene film would preclude its use in layers thick enough to significantly retard HCB flux.

Some hex waste were found to contain a dense organic liquid in which HCB is highly soluble (23,000 ug/ml). If this liquid waste drains from the waste, the potential would be created for substantial amounts of HCB to move through the soil.

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SIMULATION MODELS AND THEIR APPLICATION TO LANDFILL DISPOSAL SITING; A REVIEW OF CURRENT TECHNOLOGY

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ABSTRACT

Predicting potential groundwater pollution associated with the land disposal of liquid and solid wastes is a highly complex technological adventure. The simultaneous presence of numerous interactive mechanisms, physical, chemical as well as biological, makes it difficult to obtain an advanced picture of the possible pollution of a given waste deposited in a given geohydrological environment. Consequently, many investigators have resorted to the use of models to forecast the performance of waste disposal sites. This paper reviews some of the models currently available for such predictions. Main emphasis is thereby put on a discussion of existing conceptual-mathematical models, since these models appear the most promising but, unfortunately, also the most complex ones for evaluating groundwater pollution. An extensive list of available simulation models is given, and some of the advantages and disadvantages of these models for simulating landfill behavior are discussed.

INTRODUCTION

Whenever liquid or solid wastes are deposited on land, leachates may be generated which can seriously affect the quality of underlying groundwater systems. Predicting such groundwater pollution is a highly complex technological undertaking. The simultaneous presence of numerous interactive mechanisms (physical, chemical and biological) makes it very difficult to obtain a clear picture of the pollution potential of a given waste when deposited in a specific geohydrological environment. Many investigators have therefore resorted to the use of "models" for predicting the impact of proposed waste disposal sites. The purpose of this paper is to discuss some of the advantages and limitations of the use of "models" for such predictions. Two definitions pertinent to this discussion are given first.

A waste disposal *system* (e.g., a landfill or lagoon) is here identified with the set of physical, chemical and biological processes which act upon a number of input variables (precipitation-evaporation, amount and type of waste), and subsequently convert these into output variables (amount and type of leachate leaving the landfill, pollutant concentration in groundwater, etc.). From a management viewpoint, the waste disposal system should, in addition to the disposal site itself, also include the groundwater aquifer under and immediately downgradient of the site. A waste disposal *model* is defined as a simplified representation of the real waste disposal system. As a result of simplifications, different types of models exist. For example, a scaled-down replica of the system is as much a model of the system as is a highly sophisticated mathematical model based upon a set of partial differential equations. Even when an engineer evaluates a proposed site and uses his experience to make a decision regarding the suitability of the site for waste disposal, he most likely applies a "model" to the site. Obviously, the model in this case will be highly descriptive in nature (subjective engineering judgement is used as a decision tool).

MODEL CLASSIFICATIONS

Models can be classified in several ways. A possible classification is given below (for a more general discussion of models and simulation procedures, see Maisel and Gnugnoli, 1972, or Fishman, 1973).

1. Descriptive models. These models are expressed in one's "native language" (Emshoff and Sisson, 1970). A descriptive model results when an expert does not rely upon well-defined procedures, but uses qualitative engineering judgement to evaluate the suitability of a proposed site for waste disposal. An obvious advantage of this type of model is its low cost. The greatest limitation of a descriptive model, however, is that its predictions are very subjective and therefore difficult to communicate. Different experts may easily reach different conclusions when interpreting the model results.

2. Physical models. Physical models are those which represent scaled-down versions of the true conditions (e.g., the globe is a physical model of the earth).Unfortunatly only a few physical landfill models have been constructed in the past (Quasim, 1965; Pohland, 1975). The laboratory and scaled-down field landfills built by Drexel University in cooperation with the Pennsylvania Department of Health (Fungaroli and Steiner, 1973) represent interesting examples. The laboratory landfill was operated under controlled environmental conditions, and the field facility under natural conditions. Although these scaled-down facilities were constructed primarily to study landfill behavior as such, the field site can be viewed as a physical model for the landfill later constructed in the immediate vicinity of the experimental site. In fact, the field facility may still be regarded as a physical model for other landfills (in Pennsylvania or elsewhere), provided the geohydrological environment remains essentially the same, and similar wastes and management procedures are applied to the landfill. Generally, however, extrapolation outside the region of study is difficult due to the presence of unique local conditions (wastes, soils, hydrology, management).

Although physical models of waste disposal sites are generally lacking, many experiments can be conducted to aid the engineer in making more accurate predictions. Data may be generated, either through field or laboratory experimentation, which can be used to assess the behavior of specific waste constituents. Such experimentation may include column leaching studies to determine the rate at which certain chemicals move through a given soil, thin-layer chromatography leading also to estimates of the rate of migration of certain chemicals, or batch equilibrium studies to characterize chemical adsorption onto soils. Unfortunately, this information does not in and of itself define a waste disposal "model", and as such cannot be used as a predictive tool.

While it is obvious that scaled-down (physical) models can provide useful information about the type and concentration of chemicals expected from certain waste-soil combinations, their utility as a predictive tool appears doubtful. They are not only costly to build, but also very time-consuming to study, especially when one considers that the different chemical and biological processes within a landfill may operate over a period of several years or decades.

3. Analog models. Analog models employ a convenient transformation of a given physical system into another one which behaves in a similar manner, but which is more easily measured. The problem under investigation is then solved in the substitute state and the answer translated back into properties of the original system. Electrical analog models have found widespread application in groundwater flow modeling. Here electronic devices and properties (diodes, varistors, currents, voltages) are used to simulate groundwater flow. The analogy here, of course, is between electrical current and porous media flow. Because of the high cost of building electrical analog models for large-scale field problems, it appears doubtful that many such models will be constructed in the near future for simulating groundwater quality problems.

4. Mathematical models. Mathematical models use concise mathematical expressions for description of the physical system. Generally a set of mathematical equations is used to describe the relationships between the various system parameters and their input and output variables. Depending upon the method of analysis, this type of model may range from a few simple equations (criteria ranking) to thousands of complex mathematical expressions which can be solved only through the use of a digital computer. In the latter case, a governing set of partial differential equations is generally derived based on physical and chemical principles, and subsequently solved using either analytical

or numerical techniques. This modeling approach will be given more attention below.

In addition to the above classification, several other distinctions between models can be made, depending upon the method of analysis defined by the model and the particular approach used to solve the model. These classifications, among others, include:

1. Conceptual vs. empirical models. Models can be classified as conceptual or empirical depending upon whether or not the actual physical processes of the waste disposal system are considered. Empirical models are completely based upon observation and experimentation. The distinction between empirical and conceptual models is not always clear. Several models describing single-ion adsorption, for example, are empirical in nature (e.g., linear adsorption; the Freundlich isotherm), while others are based upon physico-chemical theory (e.g., most cation exchange equations). When column displacement experiments are carried out to measure the migration rate of certain chemicals through given soils, the approach will be empirical in nature, even though this experimention will yield parameters which are required in conceptual models (e.g., dispersion coefficients or adsorption constants). The partial differential equations describing mass transport in porous media, on the other hand, constitute a conceptual model because the governing equations are based upon principles of conservation of mass, energy and momentum. These equations, however, often use empirical relations in their derivation (adsorption, degradation, Darcy's law for fluid flow, etc.). Certain writers have used the term "black box" to indicate the empirical nature of certain models, while the terms "white box" and "synthetic model" have been used to describe conceptual models.

2. Stochastic vs. deterministic models. In a deterministic model, all input variables and system parameters are assumed to have fixed mathematical or logical relationships with each other. As a consequence, these relationships completely define the system (a unique solution is obtained). Stochastic (or probabilistic) models, on the other hand, can take into account the intrinsic randomness associated with any of the system parameters, or the uncertainties associated with the many mechanisms operating in the system, the system parameters themselves or the input variables. *Randomness* may be present because of spatial variability or medium heterogeneity. Here, certain probability distributions (normal, log-normal, etc.) are generally used to characterize the statistical behavior of the parameters in question (see for example Freeze, 1975). *Uncertainty*, on the other hand, may be present because of insufficient or unreliable input data, or because of measurement errors. Uncertainty may also result from the use of an oversimplified model. Because of an inadequate understanding of the basic physical and chemical processes in the system, different mechanisms are often lumped together, thus leading to less well-defined parameters (the dispersion coefficient is an excellent example of this). A mean and variance may then be used to describe the parameter under uncertainty (Tang and Pinder, 1977). The use of a stochastic model generally leads to a confidence interval for each of the output variables.

3. Static vs. dynamic models. This distinction depends upon how the time dimension is viewed in the model. Static models are those which evaluate steady-state conditions, i.e., where the input and output variables do not change with time. When the input and output variables do change with time, dynamic (or transient) models result. Although static models, which are much simpler and require less computational effort than dynamic models, could be used to describe certain subsystems of the waste disposal-groundwater system (e.g., for description of fluid flow in and under the disposal site), it seems that the overall system is a dynamic one and should be modeled accordingly.

4. Spatial dimensionality of the model. Although a waste disposal site and the underlying groundwater reservoir constitute a three-dimensional system, useful and accurate information can often be obtained with models which consider only one or two spatial dimensions. For example, a one-dimensional model could be used to describe the vertical transport of contaminants in the unsaturated zone between the landfill and the groundwater table. While considerable insight into the mechanisms of contaminant transport may be obtained in this way, the model stops short of providing accurate information regarding groundwater pollution of the underlying aquifer. This is because the effects of leachate dilution by flowing groundwater cannot be evaluated

with such a one-dimensional model. An exception to this obviously occurs when the water table lies far below the soil surface and when the evapotranspiration equals or exceeds the average (say yearly) precipitation. It appears that, in general, at least a two-dimensional *cross-sectional* model must be formulated. Two dimensional models may also be formulated on an *areal* basis. Here the system parameters and input and output variables represent averaged quantities along the vertical dimension.

Table 1 lists a few example models and their classification into different groups. When these models are used to evaluate the physical-chemical behavior of constituents present in a waste disposal site, including an evaluation of the potential pollution of the underlying groundwater aquifer, the model is said to simulate the waste disposal system. It is important to note here that the process of *simulation* not only includes construction of a particular model, but also its use for study of the system under consideration. As will be shown in the next section, considerable effort has been put into the development of very sophisticated groundwater quality models. Much of this effort will be wasted if these models are not used for the purpose for which they were designed (either because of their dubious practical value, their lack of testing and field verification, or the lack of familiarity of the prospective user with the capabilities of the model).

CONCEPTUAL-MATHEMATICAL MODELS

Of the different types of models discussed above, conceptual-mathematical models appear to be the most promising but, unfortunately, also the most complex ones for evaluating potential groundwater pollution from waste disposal sites. Models in this group are generally based upon a set of governing equations which are derived using well-known principles of conservation of mass, energy and momentum. After suitable simplifications, the governing equations generally reduce to a set of coupled non-linear, second-order partial differential equations, one being descriptive of fluid flow and the others characterizing the transport of the different chemical species associated with the waste leachate. The governing equations are then augmented by auxiliary conditions, describing certain system parameters (unsaturated hydraulic conductivity, ion-exchange equations, etc.) and the initial and boundary conditions imposed on the system (geometry of the landfill, aquifer characteristics, precipitation-evaporation data, location of wells or open surface water bodies, etc.).

Numerous conceptual-mathematical models are presently available, the differences between them being mostly a result of the number of simplifications made during derivation of the governing equations and their method of solution. As an example, the following partial differential equations may be used to simulate the (density independent) transport of water and dissolved constituents in a saturated-unsaturated three-dimensional medium (such as occurs in a landfill and the underlying groundwater system)

Mass transport equation.

$$\underbrace{\rho \frac{\partial S_k}{\partial t}}_{(a)} + \underbrace{\frac{\partial \theta c_k}{\partial t}}_{(b)} = \underbrace{\frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial c_k}{\partial x_j}\right)}_{(c)}$$

$$\underbrace{- \frac{\partial}{\partial x_i} (q_i c_k)}_{(d)} \pm \underbrace{\sum_{m=1}^{\ell_1} (\alpha_m \theta c_k^m)}_{(e)}$$

$$\pm \underbrace{\sum_{m=1}^{\ell_2} R_k}_{(f)} \pm \underbrace{Q c_k^*}_{(g)} \qquad (1)$$

Flow equation.

$$\left(\frac{\theta}{n} S_s + C\right) \frac{\partial h}{\partial t} = \frac{\partial}{\partial x_i} \left(K_{ij} \frac{\partial h}{\partial x_j} + K_{i3}\right) \pm Q$$

$$(i,j = 1,2,3) \qquad (2)$$

where c_k and S_k represent solution and adsorbed concentrations, respectively, of chemical species k (see Table 2 for a definition of the other symbols). The different terms in the transport equation describe the following processes: (a) changes in adsorbed concentration, (b) changes in solution concentration, (c) diffusion and dispersion effects, (d) convective transport by the fluid, (e) production (+) or decay (-) reactions, (f) additional chemical-soil or chemical-

Table 1: Some Example Models and Their Classification into Different Groups.

MODEL DEFINITION	TYPE OF MODEL				
On site inspection using engineering judgement	Descriptive	Empirical	-	Dynamic	3D*
The Drexel University experimental field landfill	Physical	Empirical	Deterministic	Dynamic	3D
Batch equilibrium study; shaker test; solid waste evaluation leachate test (subsystem models	Mathematical	Empirical	Deterministic	Static	0D
Column displacement studies; thin-layer chromatography (subsystem models)	Mathematical	Empirical	Deterministic	Dynamic	1D
Criteria listing; matrix method	Mathematical	Empirical	Deterministic	Static	0D
One-dimensional unsaturated transport model of Bresler (1973) (subsystem model)	Mathematical	Conceptual	Deterministic	Dynamic	1D
Two-dimensional saturated-unsaturated transport model of Duguid and Reeves (1976)	Mathematical	Conceptual	Deterministic	Dynamic	2D
Model for groundwater flow and mass transport under uncertainty of Tang and Pinder (1977)	Mathematical	Conceptual	Stochastic	Dynamic	2D

*) indicates spatial dimension: 3D = three-dimensional, etc.

Table 2: Explanation of Symbols Used in the Mass Transport and Flow Equations.

Symbol	Explanation
c_k	solution concentration of chemical species k (ML^{-3});
c_k^*	solution concentration of the fluid source or sink (ML^{-3});
C	specific soil moisture capacity, $C = n \frac{\partial S_w}{\partial h}$ (L^{-1});
D_{ij}	dispersion coefficient (L^2T^{-1});
h	pressure head (L);
K_{ij}	soil hydraulic conductivity (LT^{-1});
n	porosity (L^0);
q_i	volumetric fluid velocity (LT^{-1});
Q	fluid source or sink term, $Q = Q_w\ \delta(x_i - x_{wi})$ (T^{-1});
Q_w	strength of fluid source or sink (L^3T^{-1});
R_k	rate term expressing soil-chemical and chemical-chemical interactions ($ML^{-3}T^{-1}$);
S_k	adsorbed concentration of chemical species k (M^0);
S_s	specific storage coefficient (L^{-1});
S_w	degree of fluid saturation (L^0);
t	time (T);
x_i	distance in i-th coordinate direction (L);
x_{wi}	i-th coordinate of source or sink (L);
α_m	m-th order rate constant for production or decay ($M^{1-m}L^{3m-3}T^{-1}$);
δ	Dirac delta function (L^{-1});
ρ	(dry) soil bulk density (ML^{-3});
θ	volumetric moisture content (L^0).

chemical interactions (precipitation, chemical transformations, cation exchange reactions, volatilization, etc.), and (g) concentration changes resulting from fluid sources (+) or sinks (-).

Examination of equation (1) reveals that the volumetric fluid velocity q_i is required before the transport equation can be solved. For this it is necessary to also solve the flow equation. This may be done once in the case of a steady-state flow simulation ($\partial h/\partial t = 0$), or repeatedly in the case of a transient simulation. Whatever approach is used, the volumetric fluid velocity is obtained from Darcy's law as:

$$q_i = - K_{ij} \frac{\partial h}{\partial x_j} - K_{i3} \qquad (3)$$

The transport equation is also coupled to the flow equation through the dispersion coefficient, D_{ij}. The magnitude of D_{ij} depends upon the fluid flow velocity, q_i, and the soil moisture content, θ (which in turn is determined from the pressure head).

When k=1 in equation (1), transport of only a single chemical constituent is considered (e.g., chloride, a pesticide, or a trace metal). Adsorption, if present, can then be modeled by employing an equation describing the dependency of the sorbed concentration, S, on the solution concentration, c (i.e., through the use of an appropriate adsorption isotherm). Several models for adsorption and ion exchange are available for this purpose. Table 3 lists some of the most frequently used (single-ion) adsorption models. These models have been divided into two categories: equilibrium models which assume instantaneous adsorption of the chemical, and kinetic models which consider the rate of approach towards equilibrium. Not listed in the table are those models which describe competition between two ionic species, such as the commonly used cation exchange equations. Except for a few cases (e.g., model 1.5 in Table 3), generally two or more transport equations have to be solved for such multi-ion transport problems (k=2,3,...). Most of the equilibrium models in Table 3 represent special cases of the kinetic models given, and follow immediately from them by setting the time derivatives, $\partial S/\partial t$, equal to zero. All adsorption models, furthermore, represent reversible adsorption reactions, except for model 2.6. This model, used by Enfield (1974) to describe orthophosphate adsorption, represents an irreversible reaction because it does not allow for any chemical desorption (the adsorption rate is always positive).

Once the governing equations and the initial and boundary conditions are defined, solutions for the concentration can be generated by fairly straightforward, albeit very sophisticated, and tedious mathematical manipulations. Basically two approaches are currently available for this purpose: analytical and numerical methods. These two approaches are now discussed briefly.

1. Analytical methods. In order to obtain an analytical solution of the transport equation (Equation 1), one generally must assume a constant fluid velocity, a constant dispersion coefficient, constant physical parameters and a highly simplified geometry for the simulated system. Exact, usually explicit expressions for the concentration can then be generated through the use of integral and differential calculus. Although the advantages of having analytical solutions are numerous, (i.e., ease of application, and low cost of operation once derived), the necessity of having to make various simplifying assumptions severely restricts the applicability of analytical solutions to waste disposal-groundwater contamination problems. In spite of these restrictions, it appears that some of the available two- and three-dimensional analytic solutions (Kuo, 1976; Yeh and Tsai, 1976) could be applied to a few well-defined geohydrological systems, and hence should not be excluded a priori from consideration. An interesting application of this approach is also given by Larson and Reeves (1976), who describe a transport model which predicts the simultaneous flow of water and trace contaminants through a two-dimensional, unsaturated and layered soil medium.

2. Numerical methods. While some situations may lend themselves to analysis using analytical methods, most field problems have such complex physical and chemical characteristics that the flexibility of a numerical approach is required. When numerical techniques are used, the partial differential equations are generally reduced to a set of approximating algebraic equations, which subsequently are solved using methods of linear algebra. The most commonly used numerical methods are finite

Table 3: Partial List of Equations Used to Describe Adsorption Reactions [k_1 and k_2 are constants, k_r represents a rate constant (T^{-1}), and S_i and S_m represent initial and final (or maximum) adsorbed concentrations, respectively (after van Genuchten and Cleary, 1978)].

MODEL	EQUATION	REFERENCE
1. Equilibrium		
1.1 (linear)	$S = k_1c + k_2$	Lapidus and Amundson (1952) Lindstrom et al (1967)
1.2 (Langmuir)	$S = \frac{k_1c}{1 + k_2c}$	Tanji (1970) Ballaux and Peaslee (1975)
1.3 (Freundlich)	$S = k_1c^{k_2}$	Lindstrom and Boersma (1970) Swanson and Dutt (1973)
1.4	$S = k_1c\ e^{-2k_2S}$	Lindstrom et al (1971) van Genuchten et al (1974)
1.5 (Modified Kjelland)	$S = \frac{cS_m}{c + k_1(c_m - c)\exp[k_2(c_m - 2c)]}$	Lai and Jurinak (1971)
2. Non-equilibrium		
2.1 (linear)	$\frac{\partial S}{\partial t} = k_r(k_1c + k_2 - S)$	Lapidus and Amundson (1952) Oddson et al (1970)
2.2 (Langmuir)	$\frac{\partial S}{\partial t} = k_r\ (\frac{k_1c}{1 + K_2c} - S)$	Hendricks (1972)
2.3 (Freundlich)	$\frac{\partial S}{\partial t} = k_r(k_1c^{k_2} - S)$	Hornsby and Davidson (1973) van Genuchten et al (1974)
2.4	$\frac{\partial S}{\partial t} = k_re^{k_2S}(k_1c\ e^{-2k_2S} - S)$	Lindstrom et al (1971)
2.5	$\frac{\partial S}{\partial t} = k_r(S_m - S)\sinh k_2\ (\frac{S_m - S}{S_m - S_i})$	Fava and Eyring (1956) Leenheer and Ahlrichs (1971)
2.6	$\frac{\partial S}{\partial t} = k_rc^{k_1}S^{k_2}$	Enfield (1974)

differences, finite elements, and the method of characteristics.

2.1 Finite differences. When finite difference techniques are used, the partial derivatives in the governing equations are approximated by appropriate difference equations. This method has been successfully used in a number of groundwater flow problems, but its application to groundwater quality studies is limited. This is mainly due to the inability of this method to accurately reproduce irregular system boundaries, and is probably also related to the possible introduction of numerical dispersion (the artificial smearing of a concentration front) or to the presence of undesirable oscillations in calculated concentration distributions (especially when dispersive transport is small compared to convective transport). In general, however, finite difference methods are numerically the simplest to use and easiest to program, while they still can yield accurate results provided the area of interest is subdivided into a sufficiently fine grid of square or rectangular elements. Finite difference methods have found frequent application in the simulation of one-dimensional unsaturated transport problems; their application to two-dimensional problems, however, is limited.

2.2 Finite element methods. Here, the dependent variables (such as pressure head and concentration) are approximated by a finite series of basis (or shape) functions and associated, time-dependent coefficients. The approximating series are then substituted into the governing equations and the resulting errors (called "residuals") minimized through the use of weighted-residual theorems. In the Galerkin method the locally defined basis functions are the same as the weighting functions. The approximate integral equations derived in this way are evaluated using the finite element method of discretization, thereby minimizing computational effort. The domain of interest is for that purpose again subdivided into elements which, unlike for finite differences, can attain nearly any desired shape (rectangular, triangular, even elements with curved sides). Finite element methods have been successfully applied to a number of field problems involving mass transport, although in some cases the occurrence of numerical oscillations remained a problem. Main advantages of the finite element method are its flexibility in describing irregular boundaries, the ease of introducing non-homogeneous soil properties and anisotropy, and the possibility of using small elements in regions of relatively rapid change. Although the finite element method generally requires somewhat more complex numerical manipulations than finite differences, its solutions are often more accurate than finite differences if applied to the same net.

2.3. Method of characteristics. The method of characteristics, as generally used in groundwater quality simulation studies, employs a finite difference approach for solution of the flow equation, while the transport equation is solved by replacing it with a set of characteristic equations. These characteristic equations are obtained by deleting the convective transport terms from the governing equation and describing them separately. One designs for this purpose a standard finite difference net and inserts marker particles (or moving points) into each finite difference cell. The marker particles are moved through the network as prescribed by the local fluid velocities, thereby accurately describing the effects of the convective transport terms. The effects of the remaining terms in the transport equation are then superimposed on the updated positions of the marker particles by making use of the concentrations of these moving points and an appropriate finite difference scheme. The method is fairly simple in concept, and has been shown to produce acceptable results for a wide variety of field problems. An important drawback of this particular method is that it is apparently not easy to program in a general way in two or three dimensions. The resulting code is, to some extent, problem dependent.

2.4 Other numerical methods. There exists a variety of other numerical models which can be applied to groundwater contamination problems. The most primitive ones are probably those using a *lumped parameter* approach (i.e., models which do not consider any spatial variability in the dependent variables). In this approach, a mass balance equation is generally applied to the entire system, the different input and output variables being only a function of time (Hornsby, 1973; Gelhar and Wilson, 1974; Mercado, 1976). An approach incorporating more of the characteristics of a *distributive parameter* scheme may be obtained by directly applying the mass balance calculations to a number of well-defined spatial cells (elements or layers). Instantaneous mixing is often assumed within each cell, and the values of the dependent variables are identified with nodes located in the center of each element (Orlob and Woods, 1967; Tanji, 1970). A rigorous analysis of this approach shows that in this way an explicit in time finite difference approximation of the governing transport equation is obtained, provided all significant transport mechanisms are included in the mass balance equations. A very similar approach was also followed by Elzy et al (1974), who applied a "vertical-horizontal routing model" to the transport of hazardous waste products from a waste disposal site. A much more elaborate, but still somewhat similar model is the "polygonal finite difference model" of Hassan (1974). The two-dimensional elements here take the form of a polygonal network. Additional refinement of this method will eventually lead to an "integrated finite difference" approximation of the governing transport equations.

Each of the numerical techniques discussed above has a number of advantages and disadvantages associated with its use. These may be subdivided into factors affecting the accuracy, efficiency and accessibility of the particular method. While important differences in accuracy and efficiency between finite differences and finite element methods are known to exist (Pinder and Gray, 1977), it is still not quite clear to what degree these differences are important in the simulation of large field problems. In fact, it may very well be that the accuracy of the numerical technique becomes secondary when viewed against the uncertainty in the many input parameters needed in most models. Furthermore, the efficiency in programming, the general set-up of the model and its accessibility to others are as much factors determining the usefulness of the resulting program, as is the choice of the numerical technique.

SURVEY OF EXISTING MODELS

In this section, a compilation is given of the different types of conceptual-mathematical models currently available for possible use in groundwater contamination problems. The list of models, given in Table 4, is not intended to be complete; numerous other models are likely to exist, either published, unpublished or under development. The main purpose of Table 4 is to demonstrate the existence of a wide variety of models, to characterize their most important capabilities and limitations, to identify their method of solution, and to show some of their applications. The models are differentiated into four distinct groups: saturated-unsaturated transport models, saturated-only transport models, unsaturated-only transport models, and analytical transport models. Each group will be discussed briefly.

A. Saturated-unsaturated transport models. Models in this group are based directly upon equations (1) and (2), or upon appropriate simplifications of these equations. The different models simulate either a three-dimensional system (Model A4), or two-dimensional cross-sections. Except for Model A6, no cation exchange (multi-ion transport) is considered in any of the models in this group, although several do include (single-ion) adsorption and decay.

Saturated-unsaturated transport models are probably the most appropriate ones for landfill simulation because they can consider the unsaturated conditions in and under the waste disposal site. For example, aerobic decomposition of hazardous organic wastes (including pesticides) and certain oxidation/reduction reactions could be taken into account in these models. Also one of the most important "attenuation" mechanisms, dilution of leachate by flowing groundwater, can be much more clearly defined with saturated-unsaturated transport models.

Unfortunately, inclusion of the unsaturated zone also places a considerable burden on the effective and economical use of these models. The highly non-linear nature of the governing saturated-unsaturated flow equation makes its numerical solution difficult, and generally small time steps in the algorithm are necessary to ensure a correct solution. This can easily lead to extremely high computer costs when simulations are to be made over a period of several years (Segol, 1975; Duguid and Reeves, 1976). It appears that several simplifications are possible to circumvent at least some of these problems. For example, by using monthly averaged rain-evaporation data (Duguid and Reeves, 1977; van Genuchten et al (1977) rather than hourly or daily data, or by assuming only steady-state flow conditions (Sykes, 1975), one could speed up the calculations considerably. While steady-state flow conditions may be justified in a number of cases, it seems that predictions of the amount and quality of leachate interacting with the groundwater under the waste disposal site could be severely underestimated when the average evapotranspiration equals or exceeds the annual precipitation. Obviously, steady-state flow models are also unable to describe seasonal changes in the groundwater table.

An important problem associated with the use of saturated-unsaturated transport models is the need for additional input data. For example, the non-linear relationships between the hydraulic conductivity, the moisture content and the pressure head must be determined for each soil type present in the system. Expensive and time-consuming experimentation is generally required to obtain these functional relationships. In addition, and of equal importance, the difference soil-chemical interactions occurring in the unsaturated zone have to be quantified. Many of these interactions are still not fully understood and considerably more research in this area seems necessary before the full potential of these models can be utilized. A more detailed discussion of this problem is given later.

B. Saturated-only transport models. Models in this group generally ignore the dynamics of the unsaturated zone between the waste disposal site and the groundwater table. Hence, important mechanisms associated with unsaturated flow and contaminant transport cannot be considered, unless they are represented in an approximate way through data adjustments. To use these models, it is necessary to have a method of quantifying the amount and quality of leachate reaching the groundwater table. Such quantification is necessary for an accurate evaluation of the important dilution (mixing) processes operating at and immediately below the groundwater table. Given that this can be done beforehand, i.e., in a predictive way, saturated-only transport models appear to be useful tools for evaluating possible groundwater contamination. The need for describing the unsaturated zone, obviously, becomes much less when the waste disposal site is in direct contact with the saturated zone.

Saturated-only transport models have found application to a wide variety of practical field problems, often to cases where groundwater contamination was observed over a period of time and hence where calibration of the model to actual field data was possible. Unfortunately, most applications have been restricted to non-interactive (no adsorption) and single-ion transport. It seems that considerably more work is necessary to determine the accuracy of these models when applied to the transport of adsorbing chemicals.

A special class of saturated-only transport models is provided by saltwater intrusion models (Models B19-B22). These models differ from the other (cross-sectional) models in this group in that they consider density dependent flow. As such they are also directly applicable to contaminant transport from waste disposal sites.

C. Unsaturated-only transport models. Because these models consider only the unsaturated zone, they cannot be used to describe contaminant migration in groundwater systems. However, the different (mostly one-dimensional) models in this group are very useful tools for studying the mechanisms of contaminant transport in the unsaturated zone, especially the transient waste-soil interactions associated with column leaching studies. Another and very important application of these models may result when they are used simultaneously with saturated-only transport models. The unsaturated models can then be used to predict in an approximate way the amount and type of leachate reaching the groundwater table, information which subsequently can be used as input for the saturated-only transport models. Models A2 and A6 represent examples of this type of approach.

D. Analytical models. As discussed earlier, analytical models appear to have only limited application to actual (field) groundwater contamination problems. Their application is restricted to those cases wherein the geohydrology of the area is very simple (flow in one direction, constant porosity, dispersivity and conductivity). The different one-dimensional analytical solutions (Models D2) are again potentially useful tools for identification and quantification of waste-soil interactions when used in conjunction with column leaching studies (quantification of adsorption and decay constants, dispersion coefficients, etc.).

Table 4: Partial List of Published Transport Models for Application to Groundwater Quality Problems.

model references	geometry of model 1)	math. sol'n. metnod 2)	type of flow 3)	type of soil 4)	model chemistry 5)	applications/comments
A. SATURATED-UNSATURATED TRANSPORT MODELS.						
A1. Elzy, et al. (1974)	2D,C	O	Tr	-	A,D	Simple vertical-horizontal routing model for contaminant transport from a landfill.
A2. Perez, et al. (1974)	2D,C	FD	Tr	L	I	Coupled 1D vertical, unsaturated model and 2D saturated model; describes groundwater pollutio from agricultural sources.
A3. Sykes (1975)	2D,C	HFE	St	L,A	I	Contaminant transport from a landfill.
A4. Segol (1976, 1977)	3D,2D	HFE	Tr	L,A	I	Theoretical formulation only; one-dimensional verification.
A5. Duguid and Reeves (1976,77)	2D,C	LFE	Tr	L,A	A,D	Transport of radionuclides from a seepage trench; studied effects of different rainfall boundary conditions on tritium transport.
A6. Shaffer, et al. (1977)	2D,C	FD	Tr	L	A,C,D	Irrigation return flow model; coupled 1D, vertical unsaturated model, and 2D, saturated model; unsaturated model is adapted version of model C3.
A7. van Genuchten, et al. (1977), van Genuchten and Pinder (1978)	2D,C	HFE	Tr	L,A	A,D	Theoretical formulation only; applied to contaminant transport from a hypothetical landfill.
B. SATURATED-ONLY TRANSPORT MODELS.						
B1. Reddell and Sunada (1970)	2D,A,C	MOC	Tr	A	I	Three-dimensional formulation; two-dimensional application only.
B2. Fried and Ungemach (1971), Fried, et al. (1971)	2D,A	FD	Tr	-	I	Flow part based on Boussinesq equation; describes NaCl pollution from large salt dumps into alluvial aquifer in Northeastern France.
B3. Bredehoeft and Pinder (1973)	2D,A	MOC	Tr	A	I	Movement of salt water in lime stone aquifer; predicted future concentrations and tested effects of protective pumping.
B4. Robertson and Barraclough (1973), Robertson (1974)	2D,A	MOC	Tr	A	A,D	Model includes effects of linear equilibrium adsorption and linear decay; describes transport of industrial and low-level radioactive wastes into Snake River Plain aquifer, Idaho.
B5. Pinder (1973)	2D,A	HFE	Tr	A	I	Used calibrated model to predict future concentrations of hexavalent chromium seeping from waste

						disposal ponds into underlying aquifer.
B6. Konikow and Bredehoeft (1973, 1974)	2D,A	MOC	Tr	A	I	Irrigation return flow model; calibrated model was used to evaluate the effects of different irrigation practices on salinity changes in a stream-aquifer system in southeastern Colorado.
B7. Hughes and Robson (1973), Robson (1974)	2D,A	MOC	Tr	A	I	Pollution of a shallow aquifer by seepage from industrial and municipal wastes; predicted future concentrations and tested effects of alternative groundwater management practices.
B8. Ahlstrom and Baca (1974)	2D,A	MOC	St/Tr	A	A,C	Model considers adsorption and exchange of several ions.
B9. Gupta, et al. (1975)	3D	HFE	Tr	L,A	I	Simulated rising connate waters through a vertical fault in a multi-layered aquifer system (steady-state application only).
B10. Martinez, et al. (1975), Thoms, et al. (1977)	2D,A	HFE	St	-	A,D	Simulated groundwater pollution from salt dome leachates.
B11. Schwartz (1975, 1977)	2D,C	MOC	St	A	A,C,D	Hypothetical study of subsurface pollution by radioactive wastes (1975); model analysis of a proposed waste disposal site (1977).
B12. Helweg and Labadie (1976)	2D,A	MOC	Tr	A	I	Adapted version of model B6; used as a cost-effective salinity management model for stream-aquifer systems.
B13. Pickens and Lennox (1976)	2D,C	TFE	St	L,A	A	Contaminant transport from a hypothetical landfill.
B14. Besbes, et al. (1976)	2/3D,A	A/FD	Tr	L	I	Approximate areal model for multi-layered aquifer; tested effects of dam construction on salinity changes in the Kairouan plain, Tunesia.
B15. Lessi (1976)	2D,C	HFE	Tr	L	I	Applied to contaminant transport in a heterogeneous aquifer system.
B16. Cabrera and Marino (1976)	2D,C	TFE	Tr	L,A	I	Theoretical study of contaminant transport in a stream-aquifer system.
B17 Konikow (1977)	2D,A	MOC	Tr	A	I	Simulated 30-year history of groundwater pollution by chloride from unlined waste disposal ponds.

1) 1D = one-dimensional
2D = two-dimensional
3D = three-dimensional
A = areal (2D) model
C = cross-sectional (2D)

3) Tr = transient flow model
St = steady-state flow

2) A = analytical
FD = finite differences
LFE = linear finite elements
TFE = triangular finite elements
HFE = higher order/mixed finite elements
MOC = method of characteristics
0 = other methods.

4) L = layered medium
A = anisotropic medium

5) A = adsorption (single-ion)
C = cation exchange (multi-ion transport)
D = decay reactions
I = inert medium; no interactions

model references	geometry of model 1)	math. sol'n. method 2)	type of flow 3)	type of soil 4)	model chemistry 5)	applications/comments
B18. Gureghian and Cleary (1977)	3D	LFE	St	L,A	A,D	Contaminant transport from an existing landfill on Long Island, New York.
B19. Green and Cox (1966)	2D,C	MOC	St	-	I	Saltwater intrusion model.
B20. Pinder and Cooper (1970)	2D,C	MOC	St	-	I	Saltwater intrusion model.
B21. Lee and Cheng (1974)	2D,C	LFE	St	-	I	Saltwater intrusion model.
B22. Segol, et al. (1975)	2D,C	HFE	St	A	I	Saltwater intrusion model.
C. UNSATURATED-ONLY TRANSPORT MODELS.						
C1. Tanji, et al. (1967a,b), Tanji, et al. (1972)	1D	FD	St	L	A,C	Approximate finite difference solution for cation exchange in field soils.
C2. Warrick, et al. (1971)	1D	FD/A	Tr	-	I	Approximate analytical solution of transport equation; applied to field infiltration study using chloride as tracer.
C3. Dutt, et al. (1972)	1D	FD	Tr	L	A,C,D	Model considers nitrogen transformations, nitrogen uptake by crops, ion exchange and certain chemical precipitation reactions; applied to cation movement in field soils.
C4. Bresler (1973)	1D	FD	Tr	-	I	Describes chloride transport during infiltration and redistribution; compared results with field data.
C5. King and Hanks (1973, 1975)	1D	FD	Tr	-	A,C,D	Model includes water uptake by plant roots; applied to irrigation return flow quality studies.
C6. Kirda, et al. (1973)	1D	FD	Tr	-	I	Applied to anion movement in laboratory soil columns.
C7. Shah, et al. (1975)	1D	FD	St	L	A	Model assumes constant dispersion coefficient and kinetic adsorption; applied to phosphorus transport in soils.
C8. Wood and Davidson (1975) Davidson, et al. (1975)	1D	FD	Tr	-	A	Applied to pesticide transport in laboratory soil columns; model assumes chemical hysteresis in the adsorption-desorption isotherms.
C9. Bresler (1975)	2D,C	FD	Tr	-	I	Describes two-dimensional transport of solutes under a trickle source.

C10. Ungs, et al. (1976)	1D	FD	Tr	-	A	Model considers water uptake by plant roots; describes chloride transport during infiltration and redistribution.
C11. Hildebrand (1975), Hildebrand and Himmelbau (1977)	1D	FD	Tr	-	I	Simulated nitrate movement through laboratory sand columns.
C12. Selim, et al. (1976)	1D	FD	Tr	-	A	Applied to transport of 2,4-D during infiltration and redistribution.
C13. Hillel, et al. (1976)	1D	FD	Tr	-	I	Model considers water uptake by plant root system; program written in S/360 CSMP language.
C14. Jury, et al. (1977)	1D	FD	Tr	-	I	Model assumes unit gradient for pressure head in flow equation; considers water uptake by plants.
C15. Gureghian, et al. (1977)	1D	FD	Tr	L	A,C,D	Model considers multi-ion transport (ammonium, nitrite, nitrate) and non-linear adsorption.
C16. Gaudet, et al. (1977)	1D	FD	St	-	I	Model considers solute exchange between mobile and stagnant water; applied to chloride transport in laboratory sand columns.
C17. Selim, et al. (1977)	1D	FD	St	L	A	Applied to transport of chloride and 2,4-D in a two-layered soil column.
C18. Wierenga (1977)	1D	FD	Tr	-	I	Compares results obtained with transient and steady-state flow equations.
C19. van Genuchten (1978)	1D	HFE	Tr	L	A,D	Describes contaminant transport during infiltration and redistribution
D. ANALYTICAL TRANSPORT MODELS.						
D1. Cleary, et al. (1973); Kuo (1976); Yeh and Tsai (1976); Wang, et al. (1977), Cleary, (1976); among others.	2,3D	A	St	-	(A,D)	Various assumptions and applications.
D2. Lapidus and Amundson (1952); Brenner (1962); Lindstrom, et al. (1967); Lindstrom and Boersma (1971, 1973); Cleary and Adrian (1973); Marino (1974); Lindstrom and Stone (1974a, 1974b); van Genuchten and Wierenga (1976); Selim and Mansell (1976); among others.	1D	A	St	-	(A,D)	Various assumptions and applications, including: - Zero- and first-order decay; - linear equilibrium adsorption; - first-order kinetic adsorption; - solute exchange between mobile and stagnant water; - decaying boundary conditions.

DISCUSSION

The increased use of land for the disposal of a wide variety of wastes makes it necessary to have a realistic method for analyzing the effects of such disposal on the quality of underlying groundwater systems. Computer simulation models of the type discussed in the previous section may greatly aid in such an analysis, provided they are used with a clear understanding of their capabilities and limitations. The following discussion attempts to define some of the advantages and limitations associated with the use of a simulation model as a site selection tool for waste disposal systems. No attempt is made to list all possible advantages and disadvantages of a water quality (or any other) simulation model; for this the reader is referred to several recently published review papers (Coats, 1969; Weber and Hassan, 1972; Evenson et al., 1974; Holcomb, 1976; Grimsrud et al., 1976). Many of the conclusions reached in these studies are equally well applicable to the present discussion, and hence will not be restated here.

Perhaps the most important advantage of the use of a simulation model for site evaluation is that a quantitative prediction of the potential pollution of nearby groundwater aquifers can be made. For example, the shape of the contaminant plume, if present, can be described by a simulation model, while types and levels of certain contaminants at various points in the system and at different time levels can be predicted. Such predictions can be made before actual construction of the waste disposal site, and hence would provide decision makers with an advance picture of the magnitude and extent of the expected leachate migration from the site. Of course, when such evaluations are made before actual development of the site, no calibration of the model to observed field data will be possible, and hence a high degree of uncertainty will be inherent in the simulation results. This, in itself, should not limit the usefulness of a simulation model. By making several trial runs, using system parameters covering a reasonable range of uncertainty, one can still delineate the maximum and minimum extent of future groundwater contamination. In this way a model (or sensitivity) analysis of the proposed waste disposal system is obtained, which may contribute greatly to an understanding of the future behavior of the system. An excellent example of such an approach is given by Schwartz (1977), who applied a model analysis to a proposed waste disposal site for low-level radioactive wastes. The use of a simulation model for such an analysis demonstrates that they can be used as tools for site selection, but that they can never replace sound engineering judgement. Rather they can help the engineer in extracting the maximum amount of information from the available data.

Simulation models may find useful application in the effective design and management of waste disposal sites. Models can be used to match different types of wastes and disposal sites in a manner that would minimize groundwater pollution at each site. Given a certain waste, different candidate sites with different soil properties could be ranked with respect to their pollution potential. Simulation models, furthermore, can be valuable tools for determining key parameters that control the migration of leachate from a site. The presence of certain liners or impervious covers, the type and thickness of reactive earth materials beneath the waste disposal site, the thickness of the unsaturated zone, the local hydrology of the area, etc., are all factors determining the pollution potential of a given site. The effects of these factors on leachate migration are most easily assessed using appropriate (one- or multi-dimensional) simulation models. In addition, simulation models can be used to study the optimal design and location of contaminant retrieval systems. Once the waste disposal site is constructed and it is clear that unacceptable pollution is present, models could be used to determine the optimum location of wells for possible recovery of contaminants (protective pumping).

A very important application of a simulation model, not directly associated with the problem of site selection itself, is in the study of existing landfills (the model becomes now a research tool). Because many of the basic soil-physical and chemical processes operating in a waste disposal system are not very well understood, simulation of existing landfills with given waste-soil combinations may lead to a better understanding of these processes. As mentioned earlier, the one-dimensional transport models are particularly useful tools for studying the migration of contaminants in and under waste disposal sites. Such applications will undoubtedly increase our knowledge of contaminant transport (especially of adsorbing chemicals), and could eventually lead to the formulation of new theories (e.g., regarding certain adsorption mechanisms, chemical chain reactions, channeling processes, etc.)

Unfortunately, a number of limitations associated with the use of computer simulation techniques for landfill evaluation purposes also exist. Several of these limitations can be traced back to a general lack of reliable input data. A successful simulation is highly dependent upon an accurate description of the various system parameters and input variables. In particular, the two- and three-dimensional transport models, probably the most appropriate ones for landfill simulation, require considerable input data (unsaturated hydraulic conductivities, soil moisture retention curves, dispersion coefficients, adsorption and/or exchange coefficients, decay constants, etc.) It is clear that the need for such input data will greatly limit the effective and economical use of these models. Interestingly, simulation models may also find here immediate application. Because errors in different input data will not have the same effect on the calculated results, one can apply a sensitivity (or model) analysis to the proposed waste disposal site to determine those parameters which have the greatest effect. More effort can then be spent to accurately determine these parameters, while needless work and cost will be avoided by estimating the remaining ones only in a very approximate manner. As suggested earlier by Coats (1969), interest in the accuracy of the input data should be proportional to the sensitivity of computed results to variations in those data. If, for example, wide variations in the unsaturated hydraulic conductivity curve lead to only minor changes in calculated leachate migration rates, then an accurate determination of this curve seems unnecessary (actually, there exist some indications in the literature that this indeed may be the case, provided reliable estimates of the prevailing precipitation-evaporation rates at the soil surface can be obtained; see for example, Jury et al., 1977, or Wierenga, 1977).

Another problem limiting the immediate application of simulation models is associated with a lack of understanding of the many chemical and biological processes operative in a typical waste disposal site. These processes include adsorption-desorption, cation exchange, precipitation-solution, chemical chain reactions, oxidation-reduction and biodegradation. Because many of these processes are still under investigation, their quantification into reliable mathematical expressions for use in simulation models remains doubtful. For instance, it is known that there are considerable variations in quality and quantity of leachate as a function of time, probably due to an interplay between such variables as precipitation-evaporation, type and age of the waste, pH and temperature. Reliable estimates of leachate generation cannot be obtained before these interrelationships have been studied in detail and certain quantitative expressions have been established.

Many of the physical processes occurring at the waste disposal site and in the receiving groundwater aquifer are also simplified in order to complete the required simulation. For example, heterogeneities of the site and the underlying aquifer (including such processes as channeling of leachate through the waste, physical non-equilibrium due to immobile water and dead-
diffusion and adsorption, fractured flow in the aquifer, etc.) are often only included in a very approximate manner, mostly through adjustments in the value of the dispersion coefficient. Much research, also in this area, remains necessary.

CONCLUSIONS

From the discussions in this paper, it is clear that as yet no model exists that can simulate all of the physical, chemical, and biological processes that are operative in a typical waste disposal system. The question, however, arises whether or not such a model should be developed. The complexity of these processes, which operate in a simultaneous and interactive manner, are probably such that the program would be impractical. Assuming for the moment that the knowledge for such a general model is available (which it is not), and that the vast amount of input data for use in the model can be obtained (which seems unlikely) the resulting program would undoubtedly become so large and bulky that the cost of operating it would be immense.

The usefulness of a simulation model is a direct consequence of the type of questions being asked (i.e., the model should be *commensurate* with these questions). Many situations may lend themselves to analysis without an all-encompassing model. For example, several currently available models already possess the capability to describe the migration of a contaminant plume (or of TDS, chloride, BOD, etc.), and hence could find immediate application to waste disposal problems. Considerably more study is necessary for the more complex cases, such as the migration of certain trace metals or organic chemicals (both for single- and multi-ion transport). The expertise in this area is available, but it needs to be integrated into a few, relatively accurate, yet simple conceptual-mathematical models. This will require the cooperation of scientists from widely different fields (soil physicists, soil-chemists, civil engineers, sanitary engineers, geologists, mathematicians and computer scientists). A close cooperation between the computer analyst and the more experimentally inclined investigator is especially needed. A computer analyst, for example, may construct a very sophisticated, multidimensional, multi-ion transport model, only to discover that it does not work in the field or even fails to describe a single-ion column displacement experiment involving an adsorbing chemical. An experimentalist, on the other hand, may perform numerous time-consuming and expensive column leaching studies, only to discover that some simple model could have predicted many of his observations in the first place.

The list of simulation models presented in this paper shows that tremendous progress in simulation technology has been achieved in a time span of only a few years. Much research obviously remains necessary. This will likely result in a better understanding of the different mechanisms operative in waste disposal systems, and hence will lead to the construction of more efficient and reliable simulation models.

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FIELD VERIFICATION OF HAZARDOUS WASTE MIGRATION FROM LAND DISPOSAL SITES

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ABSTRACT

The vertical and horizontal migration patterns of zinc, cadium, copper, and lead through the soil and shallow aquifer systems at a secondary zinc smelter were defined by the use of soil coring and monitoring-well techniques. The migration of metals that occurred has been limited to relatively shallow depths into the soil profile by attenuation processes. Cation exchange and precipitation of insoluble metal compounds, as a result of pH changes in the infiltrating solution, were determined to be the principal mechanisms controlling the movement of the metals through the soil. Increased metals content in the shallow groundwater system have been confined to the immediate plant site.

Soil coring was determined to be an effective investigation tool, but not suitable by itself for routine monitoring of waste disposal activities. However, it should be used to gather preliminary information to aid in determining the proper horizontal and vertical locations for monitoring-well design. The analysis of water samples collected in this project generally did not provide an understandable pattern of results. A brief experiment on monitoring-well sampling indicated the need to develop reproducible sampling techniques to obtain representative water samples. The failure of some well seals in a highly polluted environment also indicates the need for additional research in monitoring-well construction.

INTRODUCTION

The primary purpose of this study was to verify in the field the effectiveness of glaciated region soils and associated surface deposits in retaining specific hazardous chemicals. The study also was designed to develop effective investigative and monitoring techniques for detecting and quantitatively evaluating the extent of groundwater pollution from surface waste disposal activities.

Special emphasis was placed on defining: 1) the vertical and horizontal migration patterns of chemical pollutants through the soil and shallow aquifer systems; and 2) the residual chemical buildup in soils in the vicinity of pollution sources. In accomplishing these goals, an understanding was developed for the practical aspects of core drilling, soil sampling, piezometer installation, and water sample collection.

Four industrial complexes were selected to study the effects of their waste disposal practices on the soils and shallow groundwater systems. For the purposes of this paper, the site where most of the time, money, and effort was spent will be discussed. This was referred to as Site A.

Site A is a secondary zinc smelter located in south-central Illinois. The plant started operations between 1885 and 1890, initially processed zinc ore, and was converted to a secondary zinc smelting facility about 1915. Wastes from the smelting operations during the first 85 years principally were heavy metals-rich cinders and ashes. During the early years large quantities of cinders were used as road fill or surfacing in the plant area. As a result of these disposal practices, there now is a 1- to 10-foot (0.30- to 3.04-m) thick layer of metals-rich cinders covering about 12 acres of the plant property.

In compliance with air pollution control regulations, a scrubber was installed on the plant stack in 1970. Prior to that time, wind-blown ash, rich in zinc and other neavy metals, was deposited on the plant site and on the surrounding farmland.

This source of pollution has now been minimized, but wastewater from the scrubber is disposed of in a seepage pit constructed on the cinder materials that form the present day land surface. Several hundred tons of high zinc content sludge have accumulated from the frequent cleaning of this pit and are being reprocessed for zinc recovery. Most of the water from the pit infiltrates into the ground underlying the plant property.

PRINCIPAL FIELD TECHNIQUES

The collection of continuous vertical core samples for geologic study and chemical analyses, and the construction of piezometers or monitoring wells for water level measurements and water sampling were the principal field techniques used in this study.

Coring

Continuous vertical core sampling was conducted with conventional Shelby tube and split spoon sampling methods through hollow stem augers. These dry drilling techniques were used to minimize the chemical alteration of samples from drilling fluids or external water sources.

Coring was done with a truck mounted Central Mining Equipment (CME) 55 and a CME 750 rig mounted on an all-terrain vehicle. The drilling crew consisted of an equipment operator and helper, assisted if necessary by the principal investigators. For the first few holes drilled, a geologist from the Illinois State Geological Survey assisted in collecting samples and made preliminary soil identifications for use in subsequent drilling.

Core Sampling

Shelby tube and split spoon samples were extruded in the field, cut into 6-inch lengths, placed in properly labeled wide mouth glass jars, and subsequently delivered to the Illinois State Geological Survey and Environmental Research Analytical Laboratory for processing and analysis. One 6-inch (15.2 cm) length of core from each 5-foot (1.52 m) segment or change in formation was taken by the drilling contractor for moisture content determination before being sent for geologic and chemical analysis.

Core Analysis

Core samples for heavy metals determinations were analyzed at the Environmental Research Analytical Laboratory with zinc as a target element. Previous experience in determining heavy metal contaminants in soil showed that digestion of a dried soil sample in 3 N HCl at slightly elevated temperatures effectively released the heavy metals without destructing the silicate lattice of the soil. The heavy metals so released were determined primarily by atomic absorption spectroscopy.

For a number of soil samples, the multi-element capability of optical emission spectroscopy was used to determine cadmium, copper, lead and zinc concentrations.

Tests using atomic absorption measurement of small spot samples from the 6-inch long samples indicated that they were too heterogeneous to permit reproducible analysis. Reproducible results were attained by homogenizing the samples and subdividing them to sample weight levels of 1 gram.

Well Construction

Analyses of water samples from observation wells has been the traditional method for monitoring groundwater pollution. To demonstrate the effectiveness of this approach and the relative cost of using wells compared with coring, a number of small-diameter (2-inch) (5.04 cm) observation wells were constructed. Since heavy metal contaminants were expected, plastic casing, screen, and pumping equipment were used.

Observation wells were constructed in the following manner. A 7-inch (17.78 cm) diameter hole was constructed, and a 2-inch diameter PVC pipe (bottom 2 feet (61 cm) slotted with a hacksaw) was placed in the open borehole. Gravel was placed from the bottom of the hole to a level about 1 foot (30 cm) above the slotted portion of the pipe. The remainder of the annulus was filled with bentonite slurry to land surface (see Figure 1).

In late February 1975, engineers from the American Colloid Company, Volclay Division, informed us of a possible problem associated with using standard sodium bentonite to seal out highly mineralized

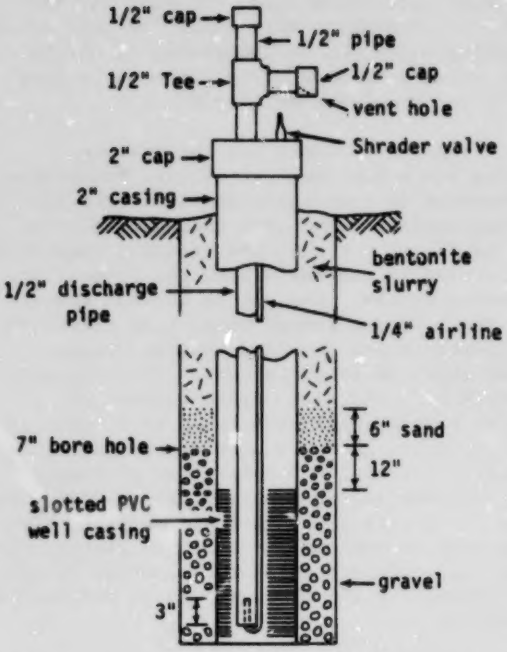


Figure 1 Typical well and pumping mechanism

waters such as those encountered in our study. They indicated that the normal swelling-sealing capability of sodium bentonite could be so seriously affected by such waters that well seal failures were almost inevitable. It was their opinion that some of our observation wells had already failed because of this factor. Water samples from shallow and deep wells were collected and submitted to American Colloid with a request for them to design a sealant mixture which would insure no leakage between aquifers.

In general, they concluded that an effective seal cannot be achieved with bentonite in an environment that is already affected by pollutants such as at this site. They suggested that monitoring wells be installed prior to disposal of waste (not always a very practical solution).

Pumping Mechanism

Observation wells were equipped with individual pumping devices to minimize possible contamination of samples from other wells. The pumping devices consisted of a 1/2-inch (1.27 cm) diameter PVC discharge pipe that extended from above the 2-inch (5.08 cm) well casing to the bottom of the well. A tee fitted with short nipples and removable caps was placed at the top of this pipe (Figure 1). The cap on the vertical segment could be removed to allow for water level measurements within the 1/2-inch pipe. The cap on the horizontal segment (water discharge outlet) was vented to permit stabilization of the water level within this pipe.

A 1/4-inch (0.63 cm) plastic airline also was installed in each well. The airline was attached to a Shrader valve at the top of the well casing and extended the entire depth of the well. The lower end of the airline was bent up into the bottom of the 1/2-inch discharge pipe for a distance of about 3 inches (7.62 cm).

Water was pumped from the wells by removing the cap from the horizontal portion of the 1/2-inch pipe and applying air to the system through the Shrader valve. Pumping from depths as great as 70 feet (21.3 m) was possible with only a bicycle-type hand pump. A gasoline powered, 4-cycle air-compressor capable of delivering about 5 cubic feet per minute (0.14 cubic meter per minute) at pressures up to 60 psi (4.2 kg/sq cm) also was used. An activated charcoal filter was placed in the airline from the compressor to insure that air from the compressor was not introducing airborne contaminants.

Since most of the wells in this study generally had a column of water less than 30 or 40 feet (9.14 or 12.19 m) deep, it was found that operating the compressor at 20 to 25 psi (1.4 to 1.8 kg/sq cm) was most effective. Higher operating pressures caused the air bubbles to rise through the water column instead of pushing slugs of water in front of them as desired. In the very shallow wells, less than 20 feet (6.1m) deep, the bicycle type hand pump actually worked more effectively.

Water Sampling

Water level measurements were made and water samples were collected from each well once a month. Water samples were collected in 6-ounce (170 grams) plastic containers and placed on ice until they were brought into the laboratory where they were refrigerated. Each well was pumped for a period of time theoretically adequate to insure that all stored water in the well casing had been removed. The wells were allowed to recover, and a sample was then collected from the water that had just entered the well. This procedure was followed in hopes that the water sample would be representative of the water flowing through the aquifer at the time of collection.

Near the end of the project a brief experiment was conducted on four wells at this site to determine if the pumping scheme just described was necessary or adequate for collecting representative water samples. Four wells were selected on the basis of early results of chemical analyses of water samples collected. Zinc concentrations in water from these wells ranged from 6.2 to 25.9 mg/l, 300 to 790 mg/l, 342 to 850 mg/l, and 12,700 to 21,580 mg/l, respectively. These values represent fluctuations in zinc content of 76, 62, 60, and 42 percent using the higher values as base concentrations.

To determine if these fluctuations were real or a function of the sampling procedure, the following experiment was conducted. Water level measurements were taken in each well and the volumes of water stored in the 2-inch diameter casings and screens were calculated. Pumping was initiated and samples were collected just after pumping began and at increments of one-half the total stored water volume until a total of 5 volumes had been pumped.

Figure 2 illustrates the results of these tests for the four wells. Percentage decreases in zinc concentrations from the first sample to the last ranged from about 45 to 78 percent with the greatest decreases occurring in the wells with the lowest zinc concentrations. Reductions in zinc content at the 1 volume pumped stage (the procedure followed in our sampling program) ranged from about 18 to 46 percent. This suggests that all of the zinc determinations of water samples collected could be as much as 30 percent higher than the stabliized zinc content beyond the 5 volume pumped stage. If the sampling procedure employed varied by even as little as 50 percent, pumping only one-half or one and one-half the stored volume, it could account for as much as 15 to 20 percent of the fluctuations in the sample results.

Additional experiments of this type should be undertaken to design satisfactory sampling procedures for other chemicals. Further, these experiments should be con-

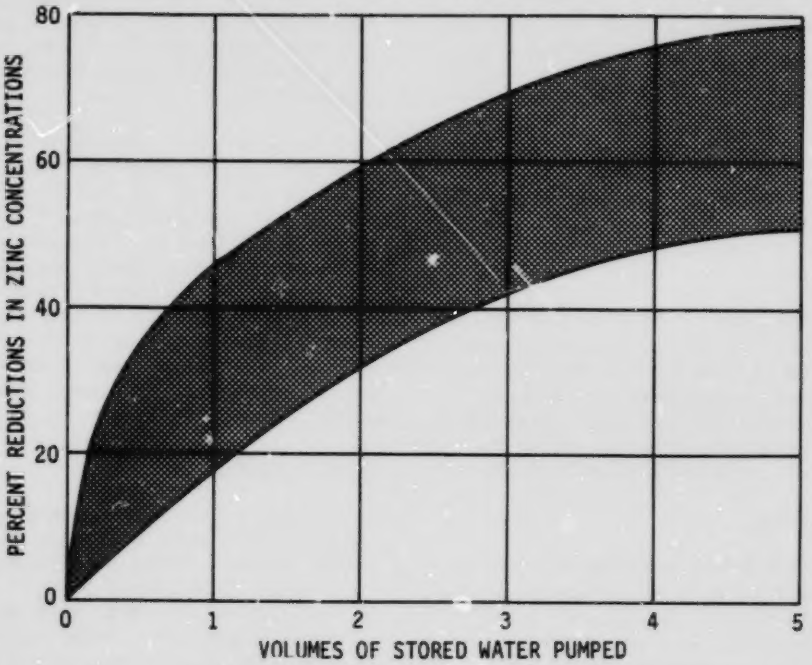


Figure 2 Effects of pumping on zinc content of water samples

ducted at the beginning of a project as opposed to near the end as in this case. The results of these brief tests indicate the need for further research in developing suitable water sampling procedures.

Water Analyses

Water samples for heavy metals analyses were analyzed at the Environmental Research Analytical Laboratory with zinc as the target element. Two electrochemical methods, anodic stripping voltammetry and pulse polarography, proved to be most effective for making zinc determinations and screening for the presence of other metals of interest. Total mineral analyses were conducted at the laboratories of the Illinois State Water Survey by standard procedures.

RESULTS

Altogether, 49 wells at 36 locations were completed at Site A. Core samples were taken at each of these locations and at an additional 23 sites (see Figure 3). Total well and core sampling footages are about 1309 and 1454 feet (398 and 443 m), respectively.

Geology

The glacial materials at this site range in thickness from about 55 feet (16.7 m) on the east to about 75 feet (22.8 m) on the west. The stratigraphic units recognized are essentially uniform in character and thickness and generally flat lying across the site. The elevation of the bedrock surface dips from 449 feet (137 m) above sea level on the east to 432 feet (132 m) on the west.

Table 1 summarizes the textual and mineralogical information for each unit. A brief description of each stratigraphic unit is as follows:

(A) Peoria Loess (4 to 6')--Brownish-gray clayey silt, non-calcareous, with iron stains.
(B) Roxanna Silt (3 to 4')--Dark brown clayey silt with up to 34 percent sand (av. 20 percent), noncalcareous Glasford Formation
(C) Berry Clay Member (3 to 4')--Dark gray sandy silty clay with trace gravel, up to 40 percent sand, noncalcareous (an accretion gley)

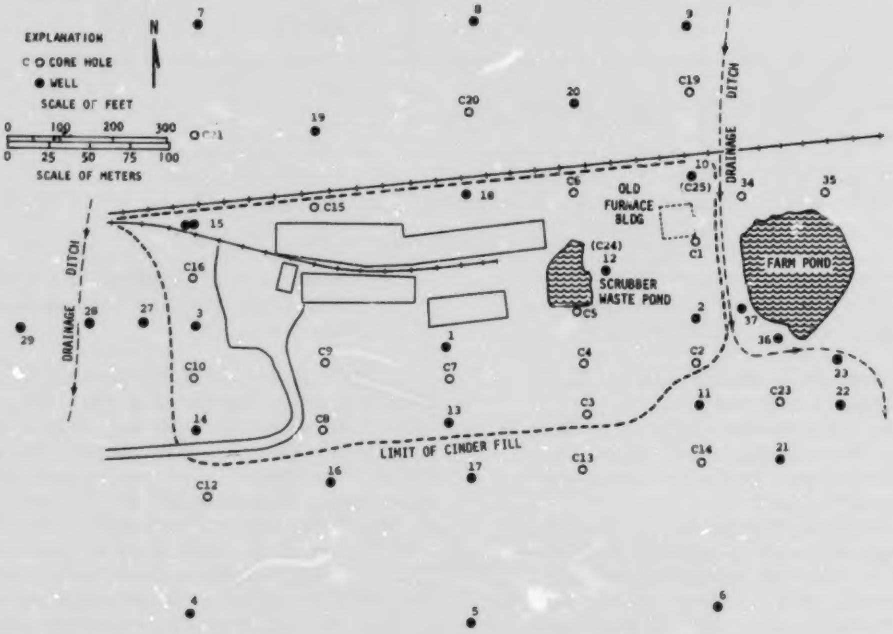

EXPLANATION
C ○ CORE HOLE
● WELL
N
SCALE OF FEET
0
100
200
300
0
25
50
75
100
SCALE OF METERS
7
8
9
C19
20
C20
19
C21
DITCH
DRAINAGE
10
(C25)
34
35
C6
OLD FURNACE BLDG
18
C15
15
C1
(C24)
12
SCRUBBER WASTE POND
FARM POND
C5
C16
DITCH
DRAINAGE
28
27
3
29
2
37
36
1
C9
C4
C2
23
C10
C7
11
C23
22
13
C3
14
C8
LIMIT OF CINDER FILL
C14
21
17
C13
16
C12
4
5
6

Figure 3 Location Map - Site A

Table 1 Textural and mineralogical data for stratigraphic units - Site A

STAGE	UNIT	AVERAGE TEXTURE	AVERAGE CLAY MINERALOGY (<2μ)	CARBONATE MINERALOGY (<2μ)
WISCONSINAN	PEORIA LOESS	(4-59-37) 10 samples	M 84.5% I 11% 8 samples	LEACHED
	ROXANA SILT	(20-47-33) 9 samples	M 85% I 8% 7 samples	LEACHED
SANGAMONIAN	BERRY CLAY MEMBER-GLASFORD FORMATION	(33-31-36) SAND INCREASES TOWARD BASE 13 samples	M 77% I 13% 13 samples	LEACHED
ILLINOIAN	HAGARSTOWN MEMBER-GLASFORD FORMATION	(46-33-21) VARIABLE 3 samples	M 30% I 51% 3 samples	LEACHED
	GLASFORD FORMATION TILL	(31-40-29) SANDIER NEAR TOP 79 samples	M 45% INCREASES WITH DEPTH I 40% DECREASES WITH DEPTH 51 samples	CONTAINS CARBONATES MAY BE LEACHED AT TOP
YARMOUTHIAN	LIERLE CLAY MEMBER-BANNER FORMATION	(24-41-35) 8 samples	M 45% I 37% VARIABLE 6 samples	LEACHED
KANSAN	BANNER FORMATION TILL	(25-44-31) SANDIER NEAR TOP 40 samples	M 16% I 55% VARIABLE 31 samples	CONTAINS CARBONATES MAY BE LEACHED AT TOP
PENNSYLVANIAN SYSTEM	BOND FORMATION	NO INFORMATION	M 3% I 4% 2 samples	LEACHED

(4-59-37) = Average percentage of sand, silt, and clay excluding gravel.

M 64% = Average percentage of montmorillonitic (expandable) minerals in clay fraction (<2μ).

I 11% = Average percentage of illite in clay fraction.

(D,E) Vandalia Till Member (2 to 8')--Yellowish brown, oxidized in upper portion, little yellowish gray at base

(F) Smithboro Till Member (25 to 31')--Dark gray sandy silt

(G) Lierle Clay Member (1 to 2')--Dark olive brown sandy silty clay, with little gravel, noncalcareous, soft. Banner Formation

(H) Unnamed Till Member (1 to 2')--Gray clayey silty till, sandy, with some gravel, mottled yellowish brown, brown and gray in upper part, strongly calcareous, hard, dry, a few scattered silt and sand lenses, predominantly dry Bond Formation (Pennsylvanian bedrock)--Greenish-gray shale with abundant mica; hard, dry

The expandable clay minerals, generally referred to as montmorillonite (M), make up more than 80 percent of the clay minerals within the Peoria Loess, Roxana Silt, and Berry Clay Member, thereby suggesting a high base exchange potential in the upper 13 feet of the materials encountered. The thin, continuous silty sand zone at the top of the Vandalia Till would appear to be the only "permeable" unit to allow groundwater to travel laterally at any moderate rate away from the site. Although there is probably some downward movement of groundwater through the remainder of the Glasford Formation, it would be expected to be extremely low.

Hydrology

On the basis of the geologic description of this site, it is quite obvious that there is no significant aquifer present in the immediate vicinity of the plant site. The Hagerstown Member, a thin (1 to 2 feet thick) continuous silty sandy zone, appears to be the only permeable zone that could allow for significant lateral groundwater movement away from the site. To develop even a domestic water supply from this sand unit probably would require the construction of two or more large-diameter bored wells.

To determine the hydrologic characteristics of this unit a pumping test with 3 observation wells was conducted at well site 2 on August 12, 1975. Well 2S (S = shallow well) was pumped for a period of 3 hours at rates from 0.180 to 0.111 gallons per minute (0.011 to 0.007 liters per second). Observation wells 1, 2, and 3 were located 7.2, 14.0, and 28.0 feet (2.19, 4.26, and 8.53 m) north of the pumped well, respectively. All drawdown data were adjusted to the final pumping rate (0.111 gpm) for analysis purposes.

The average computed coefficients of transmissivity, permeability, and storage are 285 gpd/ft (3.53 m^2/day), 190 gpd/ft^2 (7.75 m/day), and 0.00128, respectively.

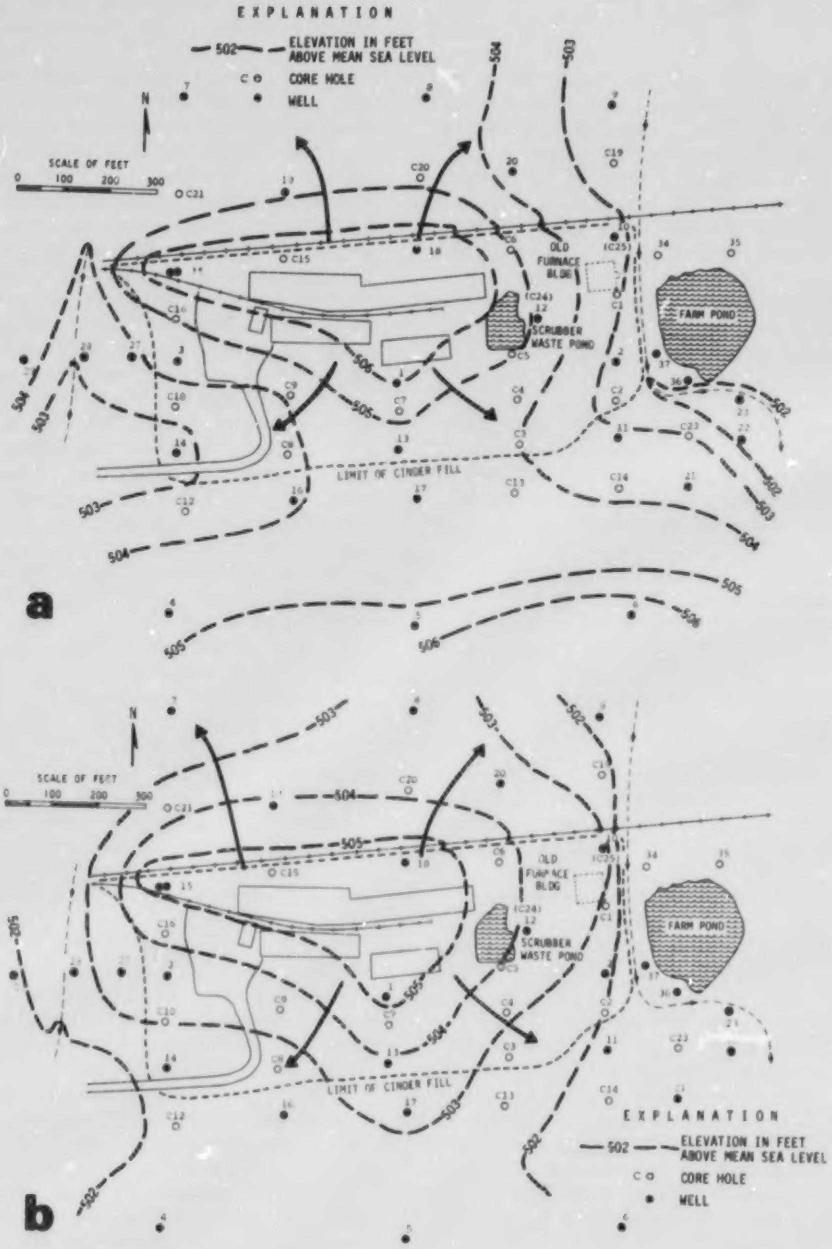
Water table contour maps were drawn for each round of water level measurements made. Figures 4a and b for March 1976 and November 1975 illustrate the high and low water table configurations, respectively. In both instances there is a water table mound beneath the plant site and movement of water is in all directions away from the plant complex. The relatively high permeability of the fill materials at the plant site, its topographic setting (higher than the surrounding land), and the liquid disposal activity at the plant all contribute to the development of this recharge mound.

Water levels for deep wells 5D (D = deep well), 6D, 7D, and 8D took approximately 15 months to stabilize. This was due to the relatively impermeable materials these wells were completed in. Wells 1D, 2D, 3D, 4D, and 9D were completed in sandier units and therefore were reflecting stabilized water levels within 1 or 2 months. Because of the slow recovery rates of some deep wells, they were not sampled monthly as were the shallow wells.

As a result of the problem of not having stabilized water levels in some of the deep wells for the period of record, monthly piezometric surface maps were not drawn. In general, water levels in the deep wells are higher than those in the shallow wells indicating a probable upward movement of water within the glacial drift sequence. In the immediate plant area, where the shallow water levels are mounded, the movement of water in the shallow deposits probably is downward and horizontally while water in the deeper units probably is moving upward and horizontally. An average apparent rate of groundwater movement in the shallow deposits was calculated for the immediate plant area with Darcy's equation v = PI where v = apparent or bulk velocity, P = permeability, and I = hydraulic gradient. The average rates of groundwater movement from the mounded area in March 1976 and November 1975 where 0.17 and 0.19 ft/day (5.2 and 5.8 cm/day) respectively. The actual or effective velocity is described by Hantush(1) as the apparent velocity divided by the effective porosity of the soil or aquifer. The effective porosity is the portion of pore space in a saturated permeable material in which flow of water takes place. Not all of the pore space of a material filled with water is open for flow, since part of the voids are filled with water that is held in place by molecular and surface water tension forces.

The porosities of the aquifer materials (Hagerstown Formation) at Site A were measured to 0.32. On the basis of data presented by Todd(2), an effective porosity or specific yield of 0.10 was assumed. With this value, effective velocities of 1.7 and 1.9 ft/day (0.52 and 0.58 m/day) or 620 to 690 ft/year (189 to 210 m/day) were calculated for the mounded area of the plant.

These unexpected high rates of movement can be explained by the relatively steep hydraulic gradients developed beneath the plant complex. Similar calculations in areas removed from the influence of the recharge mound resulted in average effective velocities of 0.15 to 0.40 ft/day (0.05 to 0.12 m/day) or 55 to 145 ft/year (16.7 to 44.2 m/yr).



EXPLANATION
502 ELEVATION IN FEET ABOVE MEAN SEA LEVEL
C ○ CORE HOLE
● WELL
N
SCALE OF FEET
0 100 200 300
OLD FURNACE BLDG
SCRUBBER WASTE POND
FARM POND
LIMIT OF CINDER FILL
502
503
504
505
506
a
b

Figure 4 Water table contour maps for a) March 1976, and b) November 1975 - Site A

Chemical Data

Aside from providing data for detailed geologic description, chemical analysis of the core samples were conducted to define: 1) the vertical and horizontal migration patterns of chemical pollutants through the soil; and 2) the residual chemical buildup in soils in the vicinity of the pollution source. Preliminary analyses of core samples during the early stages of the study indicated that four elements (zinc, cadium, copper, and lead) were most likely to be carried into the soils and groundwater system beneath the plant property. As a result these elements were selected for routine analytical analyses.

Results of chemical analysis of core samples from the Site A control hole located approximately 3 miles south-southwest of the plant, and samples from unaffected soil horizons beneath the plant property suggest that background concentrations for the four elements tested should be about 20 to 50 mg/l for zinc, 0.04 to 1.5 mg/l for cadium, 10 to 30 mg/l for copper, and 10 to 40 mg/l for lead. There appears to be no significant chemical variation with depth or between geologic unit boundaries. Some zinc levels in isolated Pleistocene soils were higher.

To outline the limits of migration of these metals beneath the plant and give an indication of the effectiveness of the soils in retaining these metals, a series of cross sections showing zinc, cadmium, copper, and lead concentrations of the soil were prepared. In figure 5 the north to south cross section illustrates that north of the railroad tracks rather small quantities of zinc were found in the upper 3 to 5 feet of the soil profile. Most of the zinc introduced into this area probably was wind blown dust and ashes from the plant stack. The area of greatest accumulation and deepest penetration of zinc in the soil occurred immediately beneath the plant property. Two principal sources of pollution, the cinders covering the plant property and the scrubber waste water, have resulted in large quantities of zinc moving into the soil profile in this area. The effect of the scrubber wastewater discharge is obvious in both cross sections. Beneath well 12 the depth of penetration (to the 100 mg/l boundary) is approximately 28 feet (3.65m). However, it is interesting to note that lateral migration due to this activity has still been very limited. It also is worth noting that no significant lateral migration has taken place beyond the two drainage ditches bounding the plant on the west and east. Farther south, beyond the limits of the cinder covered portion of the plant property, very limited zinc penetration also has occurred.

Similar cross sections illustrating the buildup of cadmium, copper, and lead are shown in figures 6, 7, and 8. The general shapes of these cross sections are similar to those for zinc. The depth of penetration of cadmium is slightly less than that of zinc but considerably greater than that of copper and lead.

The very shallow depths of penetration of these elements substantiates results of laboratory studies by Frost and Griffin(3) indicating the relative immobility of these metals. In general, the areas of greatest penetration of the four elements occurred beneath the scrubber wastewater pit where wastewater is a significant source of the metals and the recharge into the soil system is greatest. In other areas removed from the pit, the presence of the cinders becomes the dominant source and lowland areas where ponded water accumulates is the secondary source.

In addition to the direct percolation of metals-rich water at the plant site, a significant amount of metals-rich surface water is running off the plant property and percolating into the stream beds draining the plant to the southwest and southeast. An accumulation of metals-rich cinder-type sediments in the stream bed was noted. The retention of metals from the percolating water by the soil beneath the stream beds is illustrated in figure 9. The concentration of metals retained and depth of penetration decreases as the distance away from the plant site increases.

The mechanisms retaining the metals in the soil profile at Site A are predominantly cation exchange and precipitation of insoluble metal compounds as a result of pH change. Cation exchange capacity data generated indicate little variation in the retention capabilities of the upper geologic units, the silts, clays, and tills. Therefore, as metals-rich water percolates downward through the soil profile, the metals are exchanged preferentially in reverse order of their mobility.

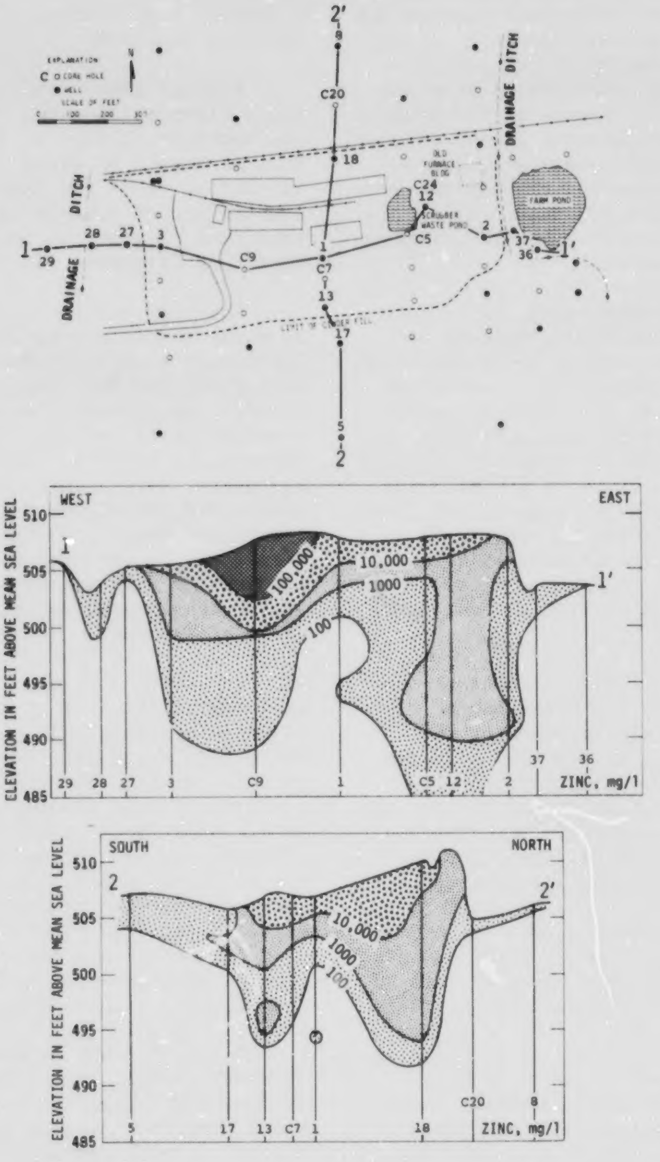

EXPLANATION
CORE HOLE
WELL
SCALE IN FEET
0 100 200 300
N
2'
8
C20
18
OLD FURNACE BLDG
C24
12
SCRUBBER WASTE POND
FARM POND
DRAINAGE DITCH
DITCH
DRAINAGE
1
29
28
27
3
C9
1
C7
13
17
C5
2
37
36
1'
LIMIT OF CINDER FILL
5
2
WEST
EAST
CLEVATION IN FEET ABOVE MEAN SEA LEVEL
510
505
500
495
490
485
100,000
10,000
1000
100
29 28 27 3 C9 1 C5 12 2 37 36
ZINC, mg/l
SOUTH
NORTH
ELEVATION IN FEET ABOVE MEAN SEA LEVEL
10,000
1000
100
5 17 13 C7 1 18 C20 8
ZINC, mg/l

Figure 5 Soil zinc concentration profiles - Site A

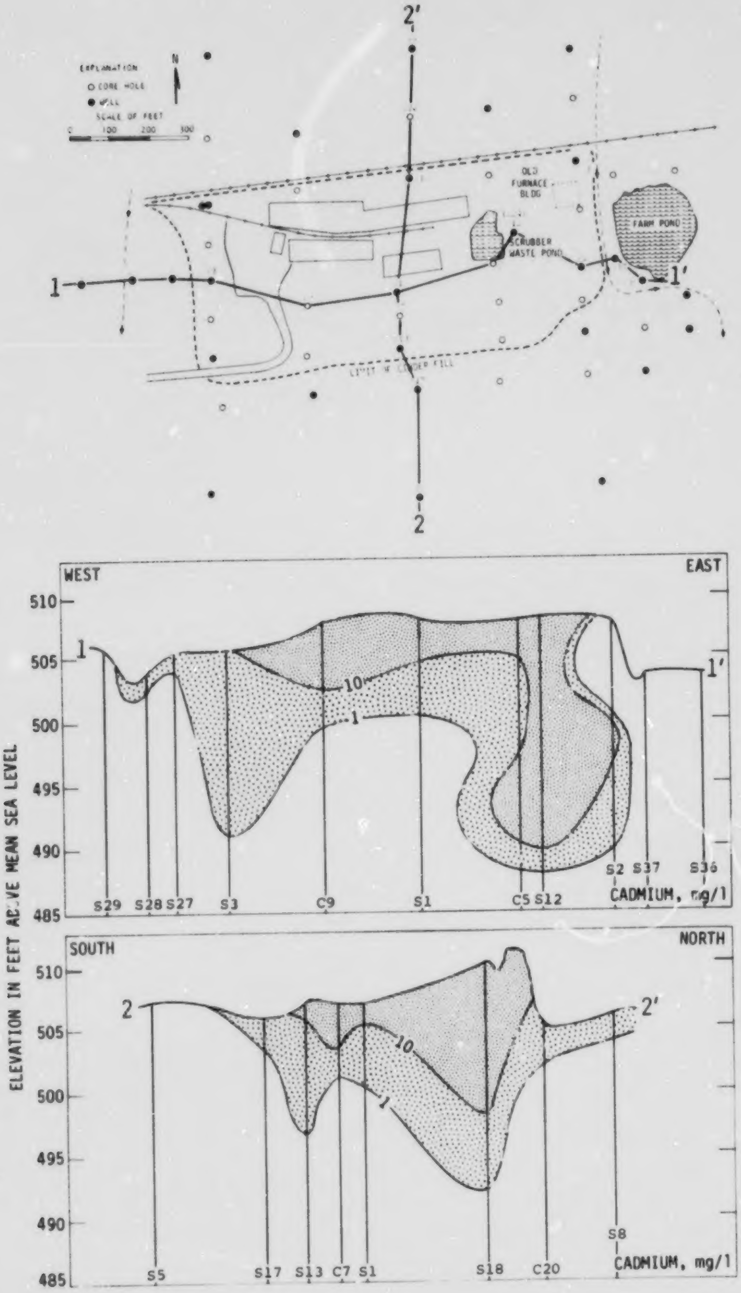


Figure 6 Soil cadmium concentration profiles - Site A

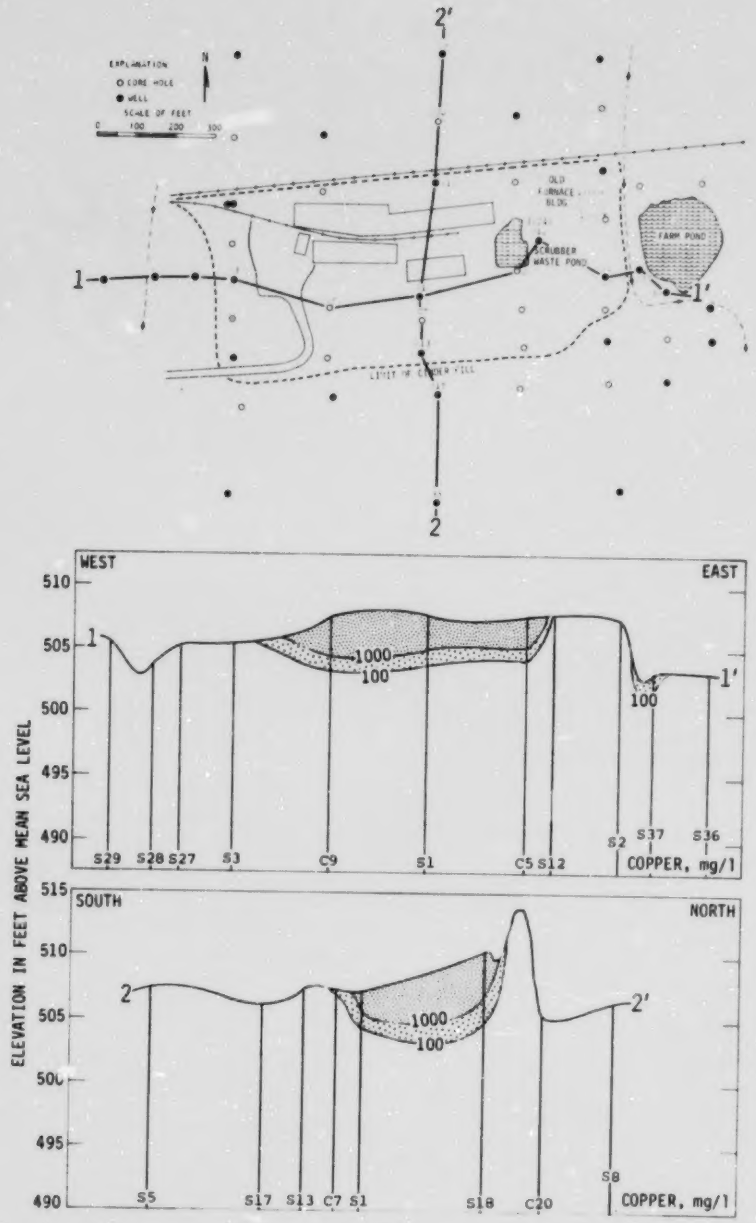

EXPLANATION
○ CORE HOLE
● WELL
SCALE OF FEET
0 100 200 300
N
2'
2
1
1'
OLD FURNACE BLDG
SCRUBBER WASTE POND
FARM POND
LIMIT OF CINDER FILL
WEST
EAST
510
505
500
495
490
1000
100
S29
S28
S27
S3
C9
S1
C5
S12
S2
S37
S36
COPPER, mg/l
SOUTH
NORTH
515
510
505
500
495
490
S5
S17
S13
C7
S1
S18
C20
S8
COPPER, mg/l
ELEVATION IN FEET ABOVE MEAN SEA LEVEL

Figure 7 Soil copper concentration profiles - Site A

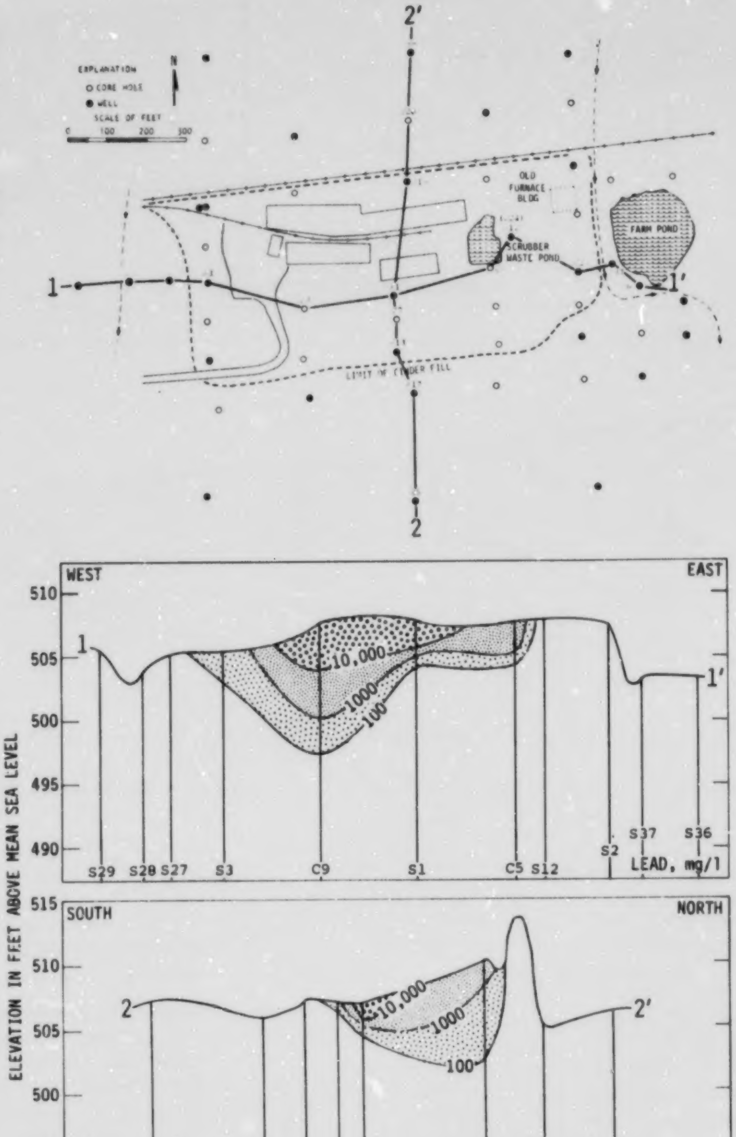


Figure 8 Soil lead concentration profiles - Site A

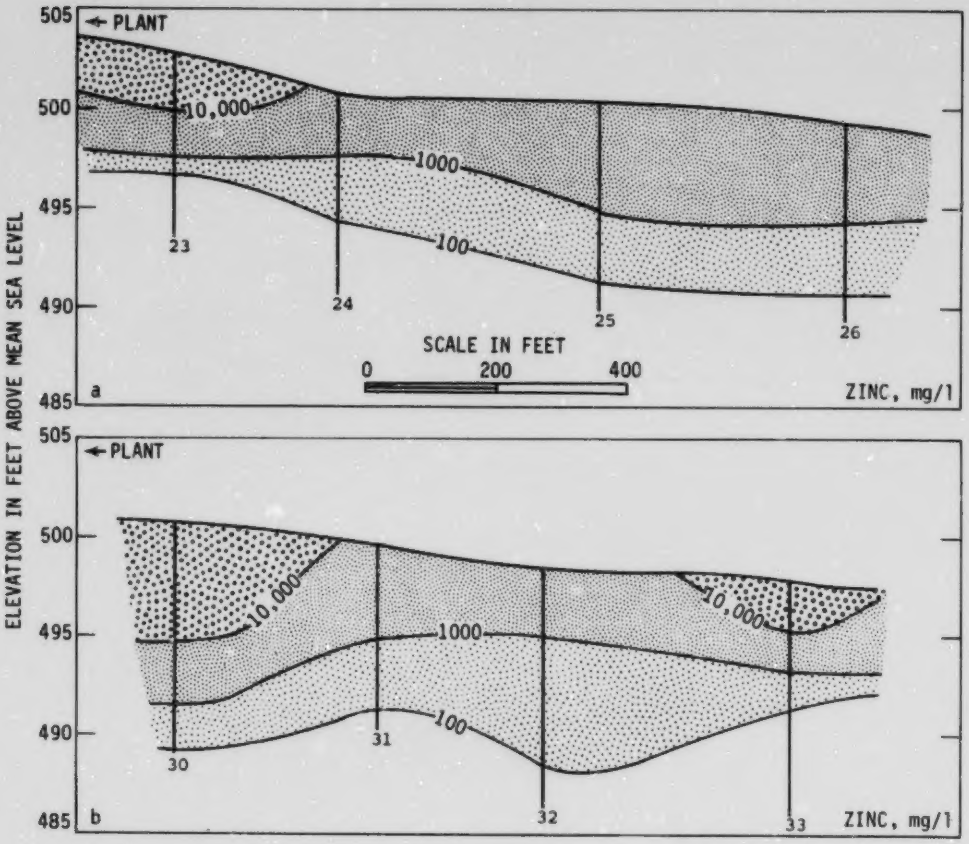


Figure 9   Streambed soil zinc concentration profiles - Site A

Cation exchange capacities (CEC) of soils measured at Site A range from about 4 to 10 me/100 grams with the larger values occurring in the shallower soils. If zinc were transferred onto the available exchange sites of the soil, cation exchange could account for soil zinc concentrations up to about 3500 mg/l. This value could be higher according to some soil specialists, because the measured CEC may be lower than the original capacity of the soil. Some researchers maintain that the soil becomes "poisoned" in the presence of pollutants and true CEC values cannot be measured.

Aside from that possibility, three other factors can be used to explain the difference between the very high soil zinc concentrations shown in the upper part of the soil profiles and the values attributable to cation exchange:

1) Some of the very high values obtained for the surface and near surface samples actually are chemical results of cinder fill samples.

2) Immediately beneath the cinder fill, fine-grained sediments from the cinders have been illuviated into the underlying soil, also resulting in high zinc values of those samples.

3) Soluble and insoluble salts of zinc and the other metals may be temporarily stored in the aerated zone waiting for eventual migration downward with later recharge events. This also results in higher zinc concentrations in soil samples from this horizon.

As the cation exchange capacity of the soil is exhausted and sufficient depth is reached to eliminate the three factors just noted, the metals buildup in the soil slowly continues to advance deeper into the soil profile. As the exchange process occurs, calcium and magnesium are released into the water from the soil and the pH of the infiltrating fluid is lowered. As the pH increases the formation of zinc precipitates results and a sharp break or decrease in soil zinc content is noted. Samples of water collected after percolating through the cinder fill materials forming the sides of the disposal pit had measured pH values near 5. It can be assumed that the same pH was experienced by water filtering downward through the cinder fill covering the plant surface. It is suspected that sulfur contained in the cinders was dissolved to form a weak sulfuric acid thus creating the low pH and increasing the mobility of the zinc.

The conclusions pertaining to the mechanism of zinc and other metals fixation drawn from this field study are in agreement with the results of recent laboratory studies by Frost and Griffin(3). They conclude that increased removal of metals from solution occurs "with increasing pH values and with increasing concentrations of the heavy metal in solution."

Chemical analysis of water collected from deep wells at Site A showed less than 0.5 mg/l zinc. The zinc contents of water collected from the shallow wells tapping the Hagarstown sand unit are illustrated in figures 10a and b. Figure 10a illustrating data for samples collected September 9, 1976, represents the maximum extent of pollution, and figure 10b illustrating data for samples collected August 13, 1975, represents the minimum extent of shallow groundwater pollution. Because the sampling procedure was not satisfactory and the attempt to detect well seal failures was unsuccessful, further analysis of the water quality data generated probably is not worthwhile. As indicated earlier, the sampling procedure used in this study could account for as much as 40 to 80 percent of the fluctuations noted between sampling periods.

To better define the quality of water in an affected and unaffected area, water samples were collected from wells 3S and 6S for total mineral analysis. The results of these analyses and the analysis of a water sample from the shallow control hole well indicate general agreement for 6S (the unaffected area well) and CH1-S. Increases in mineral constituents in the affected area well (3S) are obvious (see table 2).

The data from 3S was as expected and substantiates the solubility product calculations. The zinc concentration (750 mg/l) and pH (6.5) are in excellent agreement with the solubility of zinc hydroxide (800 mg/l at 6.5 pH).

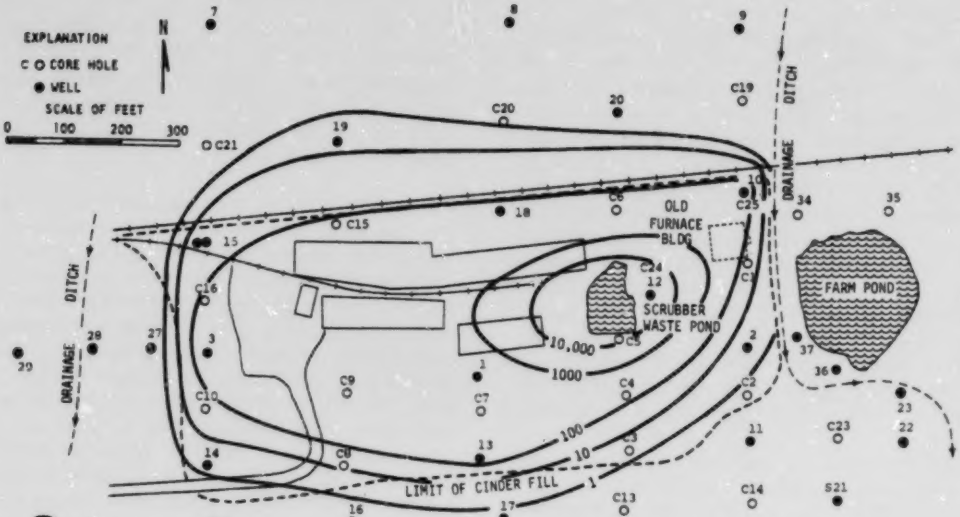
Evidence of ion exchange also is shown by the high concentrations of calcium (2400 mg/l) and magnesium (893 mg/l) present in this sample (3S). The cation exchange positions in soils in this region of Illinois are principally filled with calcium and lesser amounts of magnesium. Grim(4) indicates that zinc is higher in the montmorillonite exchange series than Ca and Mg, and thus will replace these ions on the clay structure. According to Griffin(5), this process releases calcium and magnesium to the environment even when these are not part of the original waste stream.

Because of these phenomena, it is recommended that total mineral analyses be conducted on water samples from monitoring wells where cation exchange is likely to occur. Increases in one or more of these constituents (calcium or magnesium) could be an early warning of the eventual appearance of the more toxic metals. However, to properly interpret a series of samples the problem associated with collecting comparative samples must be solved.

Summary

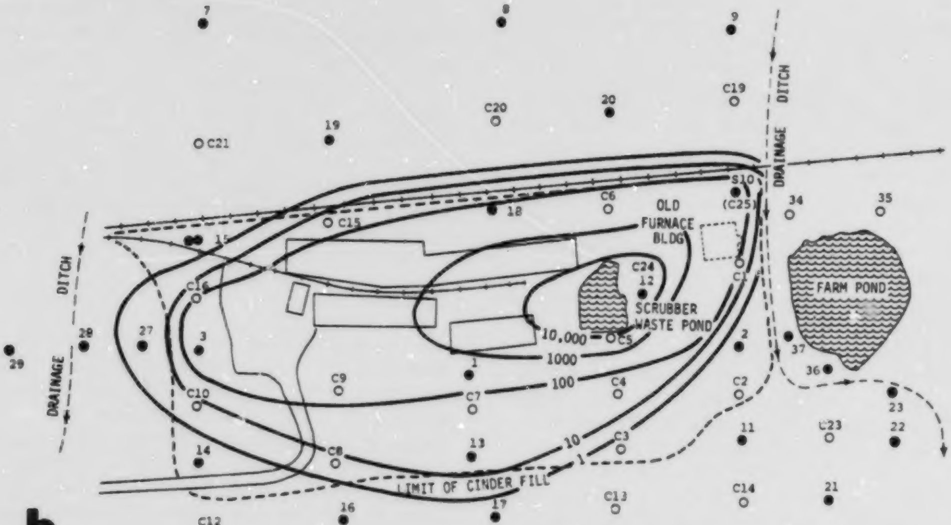
The results of soil coring and water sampling of wells at Site A have defined the migration patterns of toxic metals from this site into the ground and shallow groundwater system. Cation exchange and precipitation of metal compounds as a result of the change in pH of the infiltrating fluid are the principal attenuating mechanisms influencing the metals movement.

The geologic setting at Site A has demonstrated the ability to contain high concentrations of toxic metals over an extended length of time. The desirability of this type of geology for disposal of similar types of pollutants has been clearly demonstrated.


EXPLANATION
C ○ CORE HOLE
● WELL
SCALE OF FEET
0 100 200 300
N
DITCH
DRAINAGE
OLD FURNACE BLDG
SCRUBBER WASTE POND
FARM POND
LIMIT OF CINDER FILL
10,000
1000
100
10
1
7
8
9
C19
C20
20
19
C21
C15
18
C6
10
C25
34
35
15
C16
C24
12
C1
28
29
27
3
C5
2
37
36
1
C9
C4
C2
23
C10
C7
11
C23
22
14
C8
13
C3
C13
C14
S21
17
16
C12

a

ZINC, mg/l
SEPTEMBER 9, 1976


DITCH
DRAINAGE
OLD FURNACE BLDG
SCRUBBER WASTE POND
FARM POND
LIMIT OF CINDER FILL
10,000
1000
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7
8
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C19
C20
20
19
C21
C15
18
C6
S10
(C25)
34
35
15
C16
C24
12
C1
28
29
27
3
C5
2
37
36
1
C9
C4
C2
23
C10
C7
11
C23
22
14
C8
13
C3
C13
C14
21
17
16
C12

b

ZINC, mg/l
AUGUST 13, 1975

Figure 10 Zinc content of water from shallow wells - Site A

Table 2 Selected total mineral analyses data - Site A

		SCH1-S		S-6S		S-3S	
		mg/l	me/l	mg/l	me/l	mg/l	me/l
Iron (total)	Fe	2.3		4.7		0.0	
Manganese	Mn	.14		.44		21.01	
Calcium	Ca	96.4	4.81	33.5	1.67	2400	119.76
Magnesium	Mg	38.3	3.15	13.7	1.13	893	73.44
Strontium	Sr	.27	.01	.08		5.25	.12
Sodium	Na	75.4	3.28	81.9	3.56	389	16.92
Potassium	K	1.0	.03	0.6	.02	367	9.39
Ammonium	NH_4	0.1	.01	0.0	.00	156	8.64
Barium	Ba	<0.1		<0.1		<0.1	
Cadmium	Cd	.00		.00		1.19	.02
Chromium	Cr	.00		.00		.01	
Copper	Cu	.00		.00		.04	
Lead	Pb	<.05		<.05		<.05	
Lithium	Li	.01		.00		.15	
Nickel	Ni	<.05		<.05		2.8	.10
Zinc	Zn	.00		.04		750	22.95
Phosphate (filt)	PO_4	0.1		0.1		0.0	
Phosphate (unfilt)	PO_4	0.5		0.4		0.0	
Silica	SiO_2	15.8		13.2		33.1	
Fluoride	F	0.3		0.3		0.0	
Boron	B	0.6		0.1		0.5	
Nitrate	NO_3	0.5	.01	1.2	.02	223	3.59
Chloride	Cl	6	.17	20	.56	8300	234.06
Sulfate	SO_4	140.1	2.91	120.1	2.50	564.0	11.73
Alkalinity	(as $CaCO_3$)	404	8.08	166	3.32	40	.80
Hardness	(as $CaCO_3$)	398	7.96	140	2.80	9660	193.20
Total Dissolved Minerals		615		394		13802	

The successful application of soil coring and water sampling from wells has proven the value of these techniques as research tools. The complementary data generated from each technique are necessary to fully understand toxic metals migration.

COST ANALYSIS

Detailed cost data for collecting core samples and installing piezometers were analyzed for all sites in this study. The cost of routine core sampling in a clay environment using a professional drilling crew was $6.50 to $7.00 per foot in 1974. The cost of constructing piezometers as described in this paper was $5.00 to $6.00 per foot in 1974.

In attempting to evaluate the relative merits of soil sampling versus well installation and water sampling, the costs of analytical work and the results obtained should be considered. During the course of this study the analysis of soil samples for the four elements of interest, zinc, cadmium, copper, and lead, ran about $12.00. If a single element assay was made it ran about $7.00 Analysis of water samples for the same four elements using electric analytical techniques ran about $7.00. Single element assays ran about $5.00.

With the cost figures generated in this study some comparisons can be made. Assume that a 30-foot deep core and well is constructed. The cost of coring would be about $7.00/ft x 30 feet or $210. If analyses were made for every other 0.5-foot segment, a total of 30 samples at $7.00 each for the four elements would cost about $210. The 30-foot deep well at $6.00/ft would cost about $180. If water samples were collected monthly for one year and analyzed for the four elements of interest, the analytical work would cost about $84. The total costs of coring and analysis would be about $420 compared with $264 for a well and one year of sampling and analysis.

Depending on the type of waste to be disposed of or monitored, soil sampling may prove to be more effective even though more costly. If a research type project is being conducted, coring would prove to be most useful. The coring and analyses of the core samples give a better understanding of the phenomena that are taking place in the soil. However, due to the costs, coring may not be practical as a routine monitoring technique.

On the basis of the results of this study we recommend:

1) That coring and soil analysis be used in waste disposal research projects or in waste disposal operations when the toxicity of a waste product warrants the additional expenditure.

2) That a limited number of core samples, soil analyses, and geologic interpretations would be advisable for evaluating alternative disposal sites. Soil analyses provide a better understanding of soil interaction with the waste product than is otherwise possible, and geologic interpretation of the core samples provides better information for design and location of monitoring-wells.

3) That routine monitoring of most disposal sites should be accomplished with wells located and designed on the basis of preliminary coring analysis. Periodic coring and soil analysis may be worthwhile to substantiate original soil effectiveness assumptions.

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Adsorption, Movement, and Biological Degradation of High Concentrations of Selected Pesticides in Soils

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ABSTRACT

Equilibrium adsorption isotherms of the non-linear Freundlich type were obtained for 2,4-D amine, atrazine, terbacil, and methyl parathion and four soils from different locations within the United States. Pesticide solution concentrations ranged from zero to the aqueous solubility limit of each pesticide. The mobility of each pesticide increased as its concentration in the soil solution phase increased. These results were in agreement with adsorption isotherm data. Biological degradation of each pesticide was measured by $^{14}CO_2$ evolution resulting from the oxidation of uniformly ^{14}C ring-labeled pesticides. Technical grade and formulated material (10 to 20,000 μg/g of soil) were used. Pesticide degradation rates and soil microbial populations generally declined as the pesticide concentration in the soil increased.

The use of pesticides continues to increase despite known and suspected environmental problems and consequences. As a result, greater quantities of empty containers with pesticide residues, unused compounds which have been banned, and commercial container waste must be disposed of in an environmentally safe manner. Incineration, encapsulation, isolation in underground caves and mines, chemical stabilization, land spreading and land-fills are some of the procedures being considered for the disposal of pesticides and other hazardous wastes (1, 2). Of these methods, disposal by land-fills and land spreading appear to be the most common and economical (3, 4). Placing hazardous wastes in the soil has come under severe attack recently (5, 6) because it does not guarantee that the hazardous chemicals disposed of in this manner will not migrate from the disposal site or be degraded by soil microorganisms. An understanding of the various processes that influence microbial degradation, retention, and leaching of pesticides in soils is required before technology can be used for the selection and management of pesticide disposal sites involving soils.

The ability of a soil to degrade pesticides at low concentrations (less than 10 μg/g soil) is well established, as well as the movement of pesticides through soils at these concentrations (7, 8). However, the direct extrapolation of this data to systems containing high pesticide concentrations such as those occurring at or below disposal sites may not be feasible (9). Some pesticides have been reported to persist in soils following large applications. After five years of parathion (0,0-diethyl 0-p-nitrophenyl phosphorothioate) application to fields (30,000 to 95,000 ppm), the lowest residue level was 13,000 ppm (10). The herbicide simazine (2-chloro-4, 6-bis-ethylamino-s-triazine) for repeated annual applications of 22.4 kg/ha, persisted much longer than for annual applications of 2.8 and 5.6 kg/ha (11). Some pesticides have enhanced soil microbial activities and others have exhibited adverse effects (12, 13).

Several studies were initiated to investigate the physical, chemical, and biological processes determining the fate of pesticides in soils when applied at high concentrations. Details of these studies have been reported elsewhere (14-21); therefore, only a summary of the principal findings and conclusions are presented in this manuscript. Emphasis is given here to: (i) the influence of adsorption characteristics on pesticide mobility, (ii) measured pesticide degradation rates over a wide concentration range, and (iii) high pesticide concentration effects on soil microbial activity as measured by soil respiration rates as well as population dynamics of bacteria, fungi, and actinomycetes. The implications of the results reported here are discussed with regard to predicting the behavior of pesticides and other hazardous wastes in or around disposal sites.

MATERIALS AND METHODS

Soils

Soils used in this study were: Webster silty clay loam (Mollisol) from Iowa, Cecil sandy loam (Ultisol) from Georgia, Glendale sandy clay loam (Entisol) from New Mexico, Eustis fine sand (Entisol) and Terra Ceia muck (Histosol) from Florida. These soil types were selected on the basis of their geographic and taxonomic representation of major U. S. soils. Surface samples (0-30 cm) of each soil were air-dried and passed through a 2-mm sieve prior to storage and use. Selected physical and chemical properties of the mineral soils, are given in Table 1. Terra Ceia muck is characterized by 81% organic matter, 19% total mineral content, CEC of 350 meq/100 g and pH of 6.4.

Pesticides

Five pesticides included in this study were: 2,4-D (2,4-dichlorophenoxyacetic acid), atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine), terbacil (3-tert-butyl-5-chloro-6-methyluracil), methyl parathion (O-O-dimethyl O-p-nitrophenyl phosphorothioate), and trifluralin (α, α, α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine). Selected properties of these pesticides are given in Table 2. Stock solutions of each pesticide in 0.01 N $CaCl_2$ were prepared using the technical grade or formulated material of each pesticide. Stock solutions were made up to the aqueous solubility limit of each pesticide. A mixture of antibiotics consisting of Penicillin G and Polymixin B sulfate was added to all pesticide solutions to prevent microbial degradation during storage and use. The stock pesticide solutions were fortified with the appropriate ^{14}C-labeled pesticide compound to give specific activities in the range of 2 - 5nCi/ml.

Adsorption Experiments

Equilibrium adsorption isotherms for all soil-pesticide combinations were measured (14) using the batch procedure. Equilibrium was achieved by shaking duplicate samples of five or ten grams of soil with 10 ml of pesticide solution in pyrex screw-cap glass test tubes for 48 hours. Preliminary experiments had indicated that no measurable increase in pesticide adsorption occurred after 48 hours. Following equilibrium, the test tubes were centrifuged at 800 x G for ten minutes and the ^{14}C-activity in one-ml aliquots of the clear supernatant solution was counted by the liquid scintillation method. Decreases in pesticide solution concentration were attributed to adsorption by the soil. All adsorption experiments were performed at a constant temperature (23±1 C).

Column Displacement Experiments

Pesticide movement through water-saturated columns of soil was studied (14) using the miscible displacement technique described by Davidson et al. (22). The air-dry soil was packed in small increments into glass cylinders (15 cm long, 45 cm^2 cross-sectional area). Medium porosity fritted glass end plates served to retain the soil in the column. The soil was initially saturated with 0.01 N $CaCl_2$ solution. A known volume of pesticide solution at a desired concentration was introduced to the soil at a constant flux using a constant-volume peristaltic pump. After a specific volume of pesticide solution had been applied, the pesticide solution was subsequently displaced through the soil column with 0.01 N $CaCl_2$ at the same soil-water flux. Effluent solutions were collected in 5 or 10 ml aliquots using an automatic fraction collector. A pulse of ^3H_2O (specific activity 5 nCi/ml) was also displaced through each soil column to characterize the transport of non-adsorbed solutes. The activity of ^{14}C and ^3H_2O in ef-

TABLE 1. Physical and chemical properties of the soils used in this study.

SOIL	PARTICLE SIZE FRACTION (%) sand	silt	clay	pH (1:1 paste) Water	1N KCl	CEC (meq/100 g)	Organic C (%)	Base Saturation (%)	Extractable Acidity (meq/100 g)
Webster	18.4	45.3	38.3	7.3	6.5	54.7	3.87	91	5.15
Cecil	65.8	19.5	14.7	5.6	4.8	6.8	0.90	31	4.68
Glendale	50.7	16.4	22.9	7.4	6.5	35.8	0.50	90	3.74
Eustis	93.8	3.0	3.2	5.6	4.1	5.2	0.56	10	4.68

TABLE 2. Properties of pesticides used in this study.

Common Name	Molecular Formula	Molecular Weight	Vapor Pressure	Solubility (g/100g H_2O)	Melting Point
2,4-D	$C_6H_6Cl_2O_3$	221.0	Not determined	0.09 at 25°C	135 - 138°C (technical)
2,4-D Amine	$C_{10}H_{13}Cl_2NO_3$	266.1	1 X 10^{-10} mm Hg at 38°C	300 at 20°C	85 - 87°C
Trifluralin	$C_{13}H_{16}F_3N_3O_4$	335.3	1.99 X 10^{-4} mm Hg at 29.5°C	< 1 X $^{-4}$ at 27°C	48.5 - 49.0°C
Terbacil	$C_9H_{13}ClN_2C_2$	216.7	4.8 X 10^{-7} mm Hg at 29.5°C	0.071 at 25°C	175 - 177°C
Atrazine	$C_8H_{14}ClN_5$	215.7	1.4 X 10^{-6} mm Hg at 30°C	0.0033 at 27°C	173 - 175°C
Metyl parathion	$C_8H_{10}SPNO_6$	279.2	0.97 X 10^{-5} mm Hg at 20°C	.0055-.0060 at 25°C	36 - 36°C

fluent fractions was counted by liquid scintillation. All displacements were performed at a Darcy flux of approximately 0.22 cm/hr to ensure near-equilibrium conditions for pesticide adsorption during flow. The total volume of water held in the soil column was gravimetrically determined at the end of each displacement by extruding the soil from the glass cylinder and oven drying. The number of pore volumes (V/V_O) of solution displaced through the soil column was calculated by dividing the cumulative outflow volume (V) by total water volume (V_O) in the soil column. Effluent pesticide concentrations were expressed as relative concentrations (C/C_O), where C and C_O are, respectively, effluent and input concentration. Plots of C/C_O versus V/V_O are referred to as breakthrough curves (BTC).

Pesticide Degradation and Soil Respiration

Each soil was initially wet to a soil-water content corresponding to 30% of the 0.33 bar soil-water tension and incubated for one week at 25 C. Following incubation, each soil was then mixed thoroughly with a specific quantity of pesticide and sufficient water was added to bring the soil up to 0.33 bar soil-water tension. For pesticide degradation and soil respiration experiments, 100 gms (oven-dry basis) of each pesticide-treated soil was placed in a 250 ml Erlenmeyer flask. Special care was then taken when mixing the pesticide with the soil to ensure a uniform distribution of the pesticide within the soil. Technical grade and formulated materials of each pesticide were used. The flasks were then connected to a plexiglass manifold and CO_2-free water-saturated air passed through the manifold into the flasks at a flow rate of 10 ml/min per flask. For pesticides with a high vapor pressure, the air leaving the flask was passed through 40 ml of ethylene glycol to absorb the volatilized pesticide. The air leaving each flask was also bubbled through a KOH solution (0.1 - 0.2N) to absorb the evolved CO_2. At frequent intervals, the KOH solutions were replaced with fresh KOH solutions and the CO_2 concentrations determined by titration. ^{14}C-CO_2 activity in the KOH solution was determined by liquid scintillation counting.

Soil Microbial Activity

For the microbial enumeration experiments, 250 g of each pesticide-treated soil was placed in a 500 ml Erlenmeyer flask. Ten gram soil samples were withdrawn weekly from each flask and bacterial, fungal, and actinomycete populations determined using a dilution plate count method (18-20). The number of microorganisms were expressed as colony forming units (cfu) per gram of soil (oven-dry basis). Bacteria populations were determined using a TGY medium consisting of 5 g tryptone, 5 g of glucose, 4 g of yeast extract, 18 g of agar and 1000 mls of distilled water. The pH of the medium after autoclaving was 7.0. Bacterial colonies were counted after 48 to 52 hours at 28 C. Fungal populations were counted using a Rose Bengal-Sterptonycin agar. The pH of the fungal medium after autoclaving was 6.0. Fungal populations were determined after 60-72 hours at 28 C. Actynomycetes were plated on starch-casein agar (SC agar) supplemented with antibiotics cycloheximide 50 µg/ml and nystatin 50 µg/ml. The pH of the actynomycete medium after autoclaving was 7.2. The actynomycete colonies were counted after 12 to 14 days at 25 C.

RESULTS AND DISCUSSION

Adsorption Experiments

Equilibrium adsorption isotherms were determined for each soil-pesticide combination by measuring pesticide adsorption at five or more concentrations ranging from zero to the pesticide's aqueous solubility limit (14). An example of the type of data obtained from these experiments is presented in Figure 1. All adsorption isotherms measured were described by the Freundlich equation ($S = KC^N$); where K and N are constants, and S and C are, respectively, adsorbed (µg/g of soil) and solution (µg/ml) pesticide concentrations. The values of the Freundlich adsorption constants K and N for a given soil-pesticide combination were obtained using a least-squares fit. These values for each pesticide-soil system studied are summarized in Table 3. Because soil organic carbon content generally correlates well with pesticide adsorption, the use of an adsorption partition coefficient based upon organic carbon content rather than total soil mass was proposed by Hamaker and Thompson (23). Using this procedure, the amount of pesticide adsorbed was expressed as µg/g of organic carbon and the Freundlich constant (K_{OC}) for each adsorption isotherm was computed. These values are presented in Table 3. It is apparent that the K_{OC} values for a given pesticide are less variable among the four soils studied than are the K values uncorrected for organic carbon. These results are in general agreement with the observations of Hamaker (24) where the K_{OC} values for a given pesticide were nearly independent of soil type. It should be recognized, however, that other factors such as soil pH, clay content and cation exchange capacity may also play a significant role in determining pesticide adsorption by soils (7). On the basis of the K_{OC} values listed in Table 3, the extent of pesticide adsorption in soils was in the order of terbacil < 2,4-D amine < atrazine < methyl parathion.

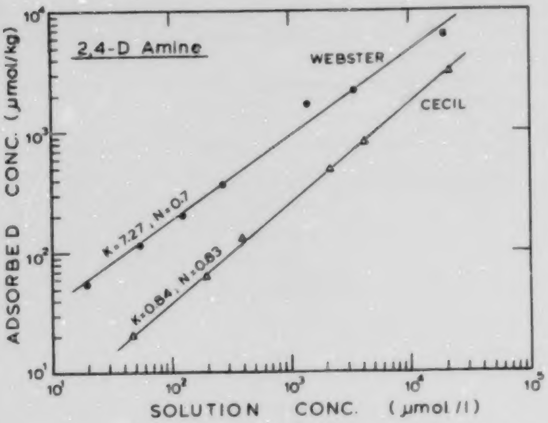

Figure 1. Adsorption isotherm for 2,4-D amine on Webster and Cecil soils. Parameters associated with each line are coefficients for Freundlich equation.

Two important conclusions can be made based on the data presented in Table 3. First, the fact that the Freundlich equation describes all pesticide adsorption isotherms studied over a wide concentration range illustrates that adsorption sites were not saturated at any concentration considered in the study. The amount of pesticide adsorbed by the soil continued to increase, at a decreasing rate, with each increase in solution concentration. This behavior may not be true for other pesticide adsorbants (25). Second, contrary to a frequent assumption, pesticide adsorption isotherms in most cases are

TABLE 3. Freundlich constants calculated from equilibrium adsorption isotherms for various soil-pesticide combinations.

PESTICIDE	SOIL TYPE	K	N	K_{OC}
2,4-D Amine	Webster	4.62	0.70	119.4
	Cecil	0.65	0.83	72.2
	Glendale	---	---	---
	Eustis	0.76	0.73	135.7
	Average ± % CV*	2.01 ± 112	0.75 ± 9	109.1 ± 30
Atrazine	Webster	6.03	0.73	155.8
	Cecil	0.89	1.04	98.9
	Glendale	0.62	0.93	124.0
	Eustis	0.62	0.79	110.7
	Average ± % CV	2.04 ± 131	0.87 ± 16	122.3 ± 20
Terbacil	Webster	2.46	0.88	63.6
	Cecil	0.38	0.99	42.2
	Glendale	0.36	0.93	76.0
	Eustis	0.12	0.88	21.4
	Average ± % CV	0.83 ± 130	0.92 ± 6	50.8 ± 47
Methyl Parathion	Webster	13.39	0.75	346.0
	Cecil	3.95	0.85	438.6
	Glendale	3.57	0.61	714.5
	Eustis	2.72	0.86	486.4
	Average ± % CV	5.91 ± 85	0.77 ± 15	496.4 ± 32

* CV is the coefficient of variation, % CV = (standard deviation/average) x 100.

non-linear, that is, N is less than one (Table 3). Linear adsorption isotherms have generally been accepted for low pesticide concentrations because it simplified computer simulation modeling (26-28). The significance of non-linear adsorption isotherms with regard to pesticide mobility in soils is discussed in the following section.

Column Displacement Experiments

Effluent breakthrough curves were measured (14) for 2,4-D amine at two input concentrations (C_o = 50 and 5,000 μg/ml) and tritiated water (^3H_2O) using water saturated Webster and Eustis soil columns (Figures 2 and 3). Tritiated water represents a non-adsorbed solute and serves as a reference for adsorbed solutes (2,4-D amine). A shift of the BTC to the right of ^3H_2O BTC is due to an adsorption-induced retardation. A greater shift of the BTC to the right indicates increased adsorption and a decreased mobility. It is apparent from the data presented in Figures 2 and 3 that the mobility of 2,4-D amine significantly increased as the input concentration of the pesticide increased from 50 to 5,000 μg/ml. Note that the 5,000 μg/ml 2,4-D amine input concentration was nearly as mobile as the ^3H_2O in the Webster soil and as mobile in the Eustis soil. The difference in mobility between the low and high 2,4-D amine concentrations was more pronounced in the Webster than in the Eustis soil. These column results are consistent with calculated retardation terms (9) obtained from the adsorption data presented in Table 3.

Breakthrough curves for the displace-

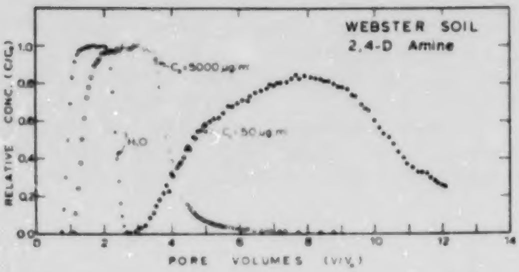

Figure 2. Effluent breakthrough curves for 2,4-D amine (C_0 = 50 and 5,000 μg/ml) and for tritiated water displaced through water saturated Webster soil column.

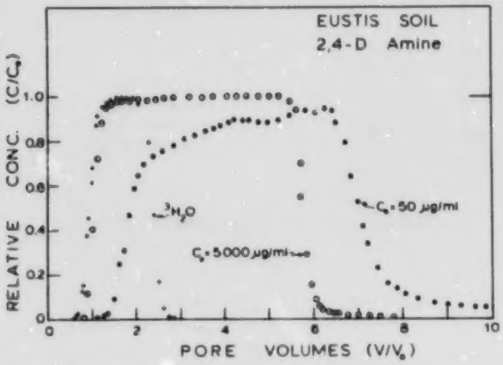

Figure 3. Effluent breakthrough curves for 2,4-D amine (C_0 = 50 and 5,000 μg/ml) and for tritiated water displaced through water saturated Eustis soil column.

ment of atrazine through a water saturated Eustis soil column at two input concentrations (C_0 = 5 and 50 μg/ml) and ^3H_2O are shown in Figure 4. The trend of increased mobility for higher atrazine solution concentrations is evident. However, the differences in atrazine mobility (Figure 4) between the two concentrations were not as large as those for 2,4-D amine (Figures 2 and 3) for a larger concentration difference. In this study, atrazine concentrations varied only by ten-fold while for the 2,4-D amine, concentrations varied by 100-fold. Also, the adsorption isotherm for 2,4-D amine in Webster soil was more non-linear than that for the Eustis soil-atrazine system (Table 3).

Pesticide Degradation and Soil Respiration

Total CO_2 evolution is generally a good indicator of soil microbial activity. This procedure was used by Stojanovic et al. (13) to study soil systems receiving high pesticide concentrations and from this pesticide degradation estimated. Because $^{14}CO_2$ evolution from uniformly ring-labeled ^{14}C-2,4-D provides a measurement of pesticide degradation, the accuracy of using total CO_2 evolution in calculating 2,4-D degradation can be compared with results obtained from $^{14}CO_2$ evolution.

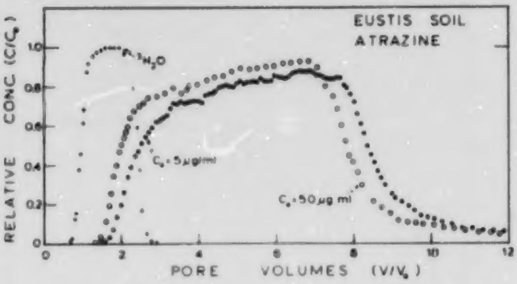

Figure 4. Effluent breakthrough curves for atrazine (C_0 = 5 and 5,000 μg/ml) and for tritiated water displaced through water saturated Eustis soil column.

The rates of CO_2 evolution from the Webster soil receiving various concentrations of technical grade and formulated 2,4-D are given in Figures 5 and 6. A common characteristic of the CO_2 evolution rate at 5,000 and 20,000 ppm of 2,4-D was the presence of two response peaks. The

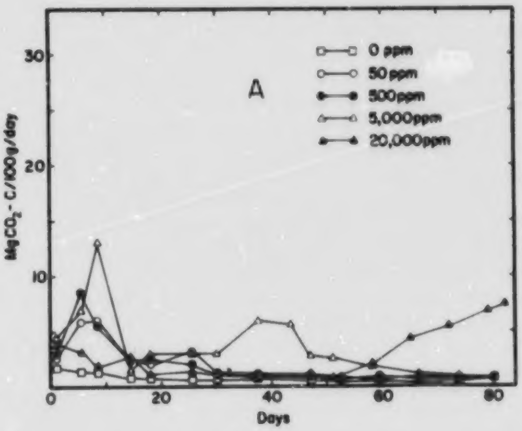

Figure 5. CO_2 evolution rate from the Webster soil receiving various concentrations of technical grade 2,4-D.

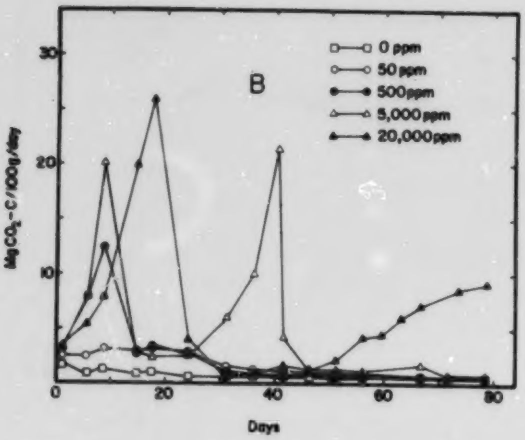

Figure 6. CO_2 evolution rate from the Webster soil receiving various concentrations of formulated 2,4-D.

initial increase in CO_2 evolution rate was followed by a decline and a second increase. This was observed for technical grade and formulated 2,4-D (Figures 5 and 6). The CO_2 carbon produced prior to the appearance of the second peak was not from the 2,4-D-carbon because very little $^{14}CO_2$ was measured during this period. For formulated 2,4-D, the CO_2-C in the first peak appeared to come from the oxidation of the formulation ingredients including dimethyl amine (Figure 6); and for technical grade 2,4-D, the CO_2-C probably originate from impurities and soil organic matter (Figure 5). The appearance of the second peak coincided with the occurrence of 2,4-D degradation ($^{14}CO_2$ evolution). Assuming all CO_2-C was evolved from 2,4-D-C, the extent of degradation during the entire experimental period (80 days) and during the second peak period was calculated. These results clearly illustrate that the majority of the CO_2-C evolved during the second peak period was primarily from the carbon in the 2,4-D. Carbon dioxide evolution rates were generally higher from the formulated 2,4-D treated soil than from the technical grade treated soil. Therefore, microbial activity in the soil receiving formulated material was higher.

Because 2,4-D degradation was determined by measuring the evolution of $^{14}CO_2$ from uniformly ring-labeled material, it can be assumed that the 2,4-D was degraded to its final oxidation products, CO_2, H_2O, and Cl^-. At concentrations of 50 and 500 ppm in the Webster silty clay loam, both forms (technical grade and formulated) of 2,4-D were mineralized rapidly to CO_2, H_2O, and Cl^- within 40 days of incubation (Figures 7 and 8). At 5,000 ppm, both forms were degraded, but exhibited lag periods of 10 to 19 days for the technical and formulated 2,4-D material, respectively.

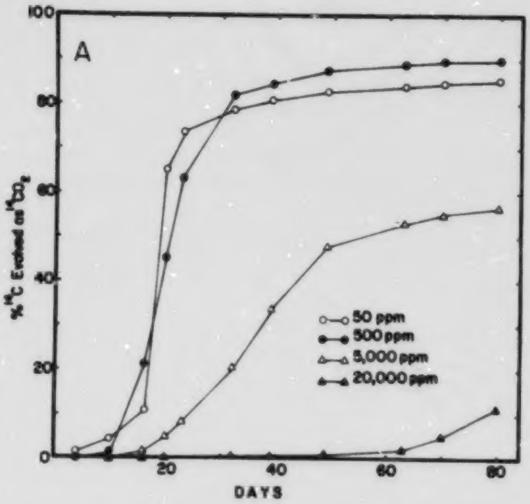

Figure 7. Percent $^{14}CO_2$ evolved from the technical grade 2,4-D treated Webster soil fortified with ^{14}C-labeled 2,4-D.

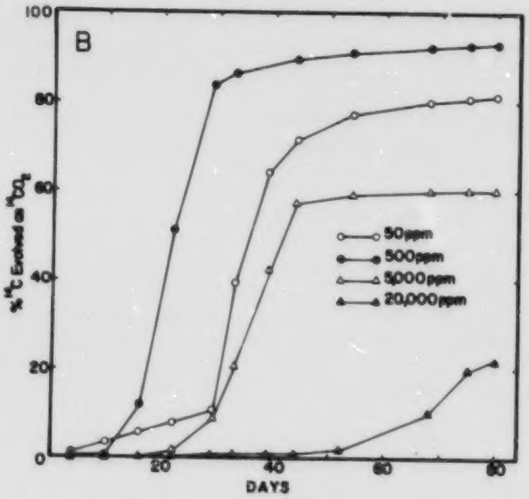

Figure 8. Percent ^{14}CO evolved from the formulated 2,4-D treated Webster soil fortified with ^{14}C-labeled 2,4-D.

No significant degradation occurred before 50 days for 20,000 ppm, and a total of 11.5% and 21.5% of the technical grade and formulated material were degraded after 80 days of incubation (Figures 7 and 8).

The CO_2 evolution rate from the untreated Terra Ceia muck soil was approximately four times higher than that from the Webster soil and eleven times higher than that from the Cecil soil. Total CO_2 evolution from the Terra Ceia muck soil treated with 5,000 and 20,000 ppm of formulated 2,4-D was high. Some of the CO_2-C produced from 5,000 ppm of formulated 2,4-D in the organic soil after seven days was from the 2,4-D-C because significant degradation occurred thereafter. For the 20,000 ppm of formulated 2,4-D treatment, total CO_2 evolution was enhanced after 36 days. This was concurrent with the degradation of 2,4-D. The CO_2 evolution rate from the Terra Ceia muck treated with 5,000 ppm of the technical grade 2,4-D increased after 20 days of incubation and coincided with a period of rapid 2,4-D degradation. Total CO_2 evolution was inhibited throughout the 80 days for 20,000 ppm of technical grade 2,4-D. Similar to the Webster soil, comparable 2,4-D degradation results were calculated where total CO_2 evolution during the second peak period rather than the entire experimental period was used.

Unlike the Webster and Terra Ceia muck soils, total CO_2 evolution was inhibited in the Cecil soil which received 5,000 and 20,000 ppm of technical grade 2,4-D as well as 20,000 ppm of formulated 2,4-D. A small stimulation was noted in total CO_2 evolution from the Cecil soil treated with 5,000 ppm of formulated 2,4-D, but no major degradation of 2,4-D occurred.

Soil respiration rates from Cecil and Webster soils receiving 10 ppm of technical grade and formulated trifluralin were not significantly different from non-treated soils except during the first week of incubation (Figures 9 and 10). Only the Webster soil data will be presented; however, soil respiration data for other soils and pesticides are discussed by Ou, et al. (17-20). Carbon dioxide evolution from the Webster soil receiving 1,000 and 20,000 ppm of technical grade trifluralin were not enhanced significantly except during the initial incubation period (Figure 9). Soil respiration rates from the Webster soil receiving 1,000 ppm of formulated trifluralin were enhanced initially, but were not different from the untreated soil during a major portion of the incubation period. For the 20,000 ppm of formulated trifluralin treatment, CO_2 evolution was stimulated whereas CO_2 evolution for this concentration in the Cecil soil was below the untreated soil.

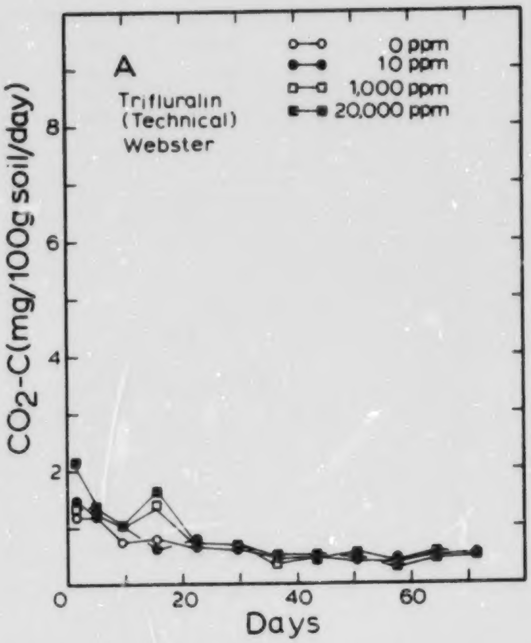

Figure 9. CO_2 evolution rate from the Webster soil receiving various concentrations of technical grade trifluralin.

Soil Microbial Activity

Bacterial populations in the 10 ppm trifluralin treated (technical grade and formulated) Webster soil were not significantly different from the untreated soil. This is in agreement with the soil respiration data presented in Figures 9 and 10. However, bacterial populations in the Webster soil receiving 1,000 ppm of formulated trifluralin were consistently higher than the untreated soil with the greater stimulation occurring in the Cecil rather than the Webster soil. For 20,000 ppm of technical grade trifluralin, the bacterial populations in the Cecil soil were stimulated but not in the Webster soil. The bacterial populations in the Cecil soil receiving

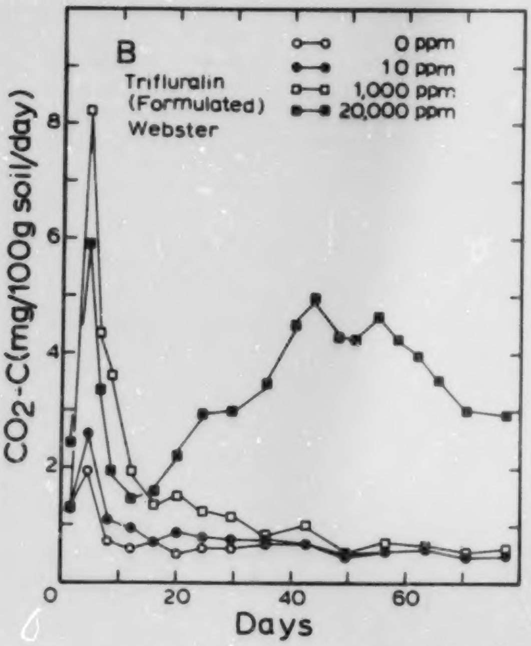

Figure 10. CO_2 evolution rate from the Webster soil receiving various concentrations of formulated trifluralin.

20,000 ppm of formulated trifluralin were initially inhibited, but were enhanced significantly after 2 weeks of incubation; whereas bacterial populations in the Webster soil for the same treatment were stimulated during the first 18 hours and continued to increase throughout the incubation period.

Fungal populations in the Cecil and Webster soils treated with 10 ppm of technical grade and formulated trifluralin were generally not significantly different from the untreated soil. For the 1,000 ppm treatments, fungal populations in the Cecil soil receiving technical grade and in the Webster soil receiving formulated trifluralin were not significantly affected, whereas the Cecil soil treated with the formulated material and the Webster soil with the technical grade material showed a significant effect at the 0.01 and 0.05 levels, respectively. The fungal populations were significantly reduced in both soils at 20,000 ppm of formulated trifluralin; whereas fungal populations in the Webster soil receiving the technical grade material were stimulated during the first four weeks.

Actinomycete populations in Cecil and Webster soils receiving 10, 1,000 and 20,000 ppm of trifluralin (technical grade or formulation) were not, in general, significantly different from the untreated soils.

CONCLUSIONS AND SUMMARY

The increased pesticide mobility at high concentrations limits the usefulness of the present low concentration data base for developing safe management practices for pesticide disposal in soils. However, underestimation of pesticide mobility by assuming linear adsorption isotherms may be less severe for pesticides with low aqueous solutilities. Ou et al. (17, 18) show that for high pesticide loading rates, up to 20,000 μg 2,4-D/g soil, there was a significant decrease in pesticide degradation rate with an accompanying depression of total microbial activity in the soil. Thus, due to rapid leaching and minimal microbial decomposition at high 2,4-D concentrations, the potential for groundwater pollution exists. The results presented in this manuscript may also be applicable when describing the behavior of other hazardous wastes applied to soils.

Microbial populations (especially bacteria) in the Webster soil were nearly twice that in the Cecil soil. The Webster soil had a higher organic matter and clay content than the Cecil soil as well as a neutral pH. High organic matter and clay contents provide larger surface area which enhance pesticide adsorption and reduces the toxicity of the applied pesticide. The results presented here are not consistent with those of Stojanovic et al (9); however, this should not be surprising owing to differences observed in the behavior of different soils and pesticide forms. The results presented in this study suggest that disposal of trifluralin and atrazine wastes in soils may not drastically reduce soil microbial activity, and in fact may enhance it under some situations. However, long term effects under field conditions remain unanswered. The fact that the microbial populations were stimulated by pesticide application, as inferred from enhanced soil respiration, does not necessarily mean that pesticide degradation has occurred. Certain precautions should be made in evaluating pesticide degradation data based on soil respiration (i.e., total CO_2 evolution) as the only measurement of pesticide degradation.

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MODELLING CONTAMINANT ATTENUATION IN SOIL: MICROBIAL DECOMPOSITION OF ORGANIC MATTER

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ABSTRACT

An investigation was undertaken to examine the microbial decomposition of organic matter in soil. Sealed saturated soil columns received a continuous upflow of laboratory lysimeter leachate at a Darcy velocity of 1.54 cm/day. After 70 days of operation, the influent COD of 5700 mg/ℓ had been reduced by 90% over the 41 cm soil column length. Methane production was vigorous. A carbon balance across the column showed 94% recovery of influent carbon. Monod-type equations combined with expressions for advection and dispersion were used in a model to simulate column effluent COD concentrations. Biological parameters taken from reports external to this study yielded good simulation under the operational conditions used. Guidelines were provided for applying the results to other situations including the disposal of industrial wastes in soil.

INTRODUCTION

The microbial decomposition of organic matter is a subject which has received little attention in research on contaminant movement in soil. This is peculiar in view of the high concentration of organic matter frequently reported for landfill leachates and certain industrial liquids released to soil/groundwater systems for disposal.

The concentration of organic matter with respect to water pollution has traditionally been determined by non-specific measurements such as biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC). In some cases more specific measurements for components such as volatile acids and trace organics have been used. An example of the latter is polychlorinated biphenyls (PCB).

The concentration of organic matter in landfill leachate varies from site to site but in many cases is quite high. Concentrations of COD have been reported in excess of 70,000 mg/ℓ(1) although this appears to be near the upper limit for leachates. Concentrations between 20,000 and 50,000 mg/ℓ have been reported on several occasions (1,2,3,4). These reports have dealt mostly with simulated landfill conditions and/or rates of infiltration well above field rates. This has usually been accompanied by acid pH in the range of 5 to 7, indicating that the anaerobic processes occurring in the landfill have been weighted heavily on the side of fermentation with volatile acid release well in excess of methane production (5,6).

For in situ landfills receiving natural precipitation, COD's tend to range up to 20,000 mg/ℓ depending on site age with pH slightly acidic to neutral (4,7,8). Methane production is often active at these sites.

As landfills age, leachate COD's tend to reduce. However, the work of Hughes et al.(8) showed that leachate COD's in the 1000's were common at Northeastern Illinois landfills ten to fifteen years after placement. Consequently, the landfill represents a significance source of organic contaminants for many years.

In contrast however, at many landfill sites, high concentrations of organic matter tend not to appear in adjacent groundwaters. It is clear therefore, that other attenuating processes work to reduce the concentration of leachate organics, possible processes being dispersion, sorption onto soil and microbial decomposition.

Dispersion during migration reduces leachate component concentrations, the extent being represented by changes in chloride ion (Cl) concentrations down flow. However, reductions in organic matter concentrations exceed those observed for Cl (7,8) and thus other mechanisms are operative.

From the limited data available (9,10), the sorption of leachate organic matter onto soil is not extensive although it does vary with organic matter and soil type.

While little evidence is available to support its existance, the microbial decomposition of leachate and other organic matter in soil appears to be a significant attenuating force. Consequently, this work was undertaken to investigate:

1. the extent and rate of organic matter reduction and factors affecting them
2. the types of organic matter reduced
3. the production of gaseous by-products and
4. the development of models for simulation.

EXPERIMENTATION

Two parallel experiments, R-2 and R-3 were conducted on a laboratory scale using packed soil columns operated anaerobically under continuous saturated flow conditions. The properties of the silty sand soil in place are shown in Table 1 for column R-2. Permeability measurements based on constant head experiments are given before and after experimentation and show only a slight reduction resulting from 120 days of microbial activity.

A schematic representation of the columns is shown in Figure 1. Upflow conditions under positive head ensured saturated flow. Liquid addition under constant head was continued throughout the experiments. Anaerobiosis was achieved by sealing the system, maintaining the gases as produced above all liquid surfaces and flushing appurtenances with nitrogen after each feed addition.

TABLE 1

SOIL COLUMN PROPERTIES

soil depth	40.6 cm
soil surface area	76.5 cm^2
D_{10}	0.012 mm
D_{60} / D_{10}	1.75
permeability : (initial) (120 days)	 1.3×10^{-3} cm/sec 1.1×10^{-3} cm/sec
porosity	0.35
organic content	0.66 % dry weight
cation exchange capacity	2.03 meq/100 gm

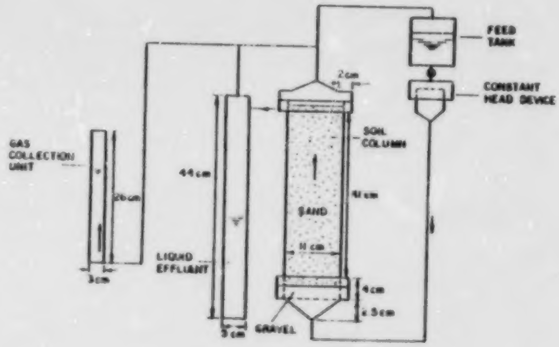

FIGURE 1

SCHEMATIC DIAGRAM OF SOIL COLUMNS

LIQUID ADDITION

The liquid used was simulated landfill leachate produced through moisture addition to residential solid waste in a laboratory lysimeter (2). Its properties are summarized in Table 2. It was characterized by high concentrations of organic matter, in particular free volatile fatty acids and an acidic pH which showed it to be typical of lysimeter leachate (1,3). The free volatile fatty acids detected consisted mainly of acetic, propronic and n-butyroc acids and accounted for 54% of the TOC as compared to 61% reported by Chian and DeWalle(1). The balance of the TOC was not identified but was assumed to consist in part of additional fatty acids, nitrogen containing compounds (ORG-N = 147 mg/ℓ) in addition to fulvic and humic-like materials (1).

TABLE 2

LEACHATE PROPERTIES

pH	5.7	
COD	39 000	mg/ℓ
TOC	11 600	mg/ℓ
free volatile fatty acids:		
acetic	3810	mg/ℓ
propionic	1640	mg/ℓ
isobutyric	590	mg/ℓ
n-butyric	4880	mg/ℓ
isovaleric	870	mg/ℓ
n-valeric	240	mg/ℓ
Σ	12 030	mg/ℓ
	(54 % of TOC)	
PO_4^{3-} - P	4.7	mg/ℓ
NH_3 - N	1134	mg/ℓ
ORG - N	147	mg/ℓ
Cl^-	895	mg/ℓ

The stoichiometry and minimum nutritional requirements of methanogenic bacteria are shown in Table 3 (5,11) along with information on COD: total P ratios for various leachates. The requirement for P is modest at a COD: P ratio of 1250:1 since much more of the organic matter is devoted to electron reception than is the case for aerobic populations. Notwithstanding however, the leachate of this study and of certain others as well, are shown to be P deficient.

In addition, the P requirements above relate to minimum growth. They do not address the need for additional P to increase growth rates above the minimum level.

TABLE 3

NUTRIENT REQUIREMENTS OF METHANOGENIC BACTERIA (M^c CARTY, O'ROURKE)

Cell Formula = $C_{62.5} H_{112.5} O_{37.5} N_{12.5} P_1$

Minimum Yield Coefficient = 0.04 mg VSS/mg COD

COD : N : P = 100 : 0.44 : 0.08

COD : P = 1250 : 1

P AVAILABILITY

Leachate Source	COD : P
Dupage LW5B (8); landfill, natural H_2O	6670 : 1
Mission Canyon (12); " , " "	4680 : 1
Boone County (12); test cell, " "	630 : 1
Sonoma County (4); landfill, high H_2O	3420 : 1
Illinois (1); lysimeter	710 - 2250 : 1
Waterloo (2); lysimeter	8300 : 1

In order to encourage growth in this study, conditions were improved, through the addition of 40 mg/ℓ P to the leachate in the form of phosphate ion (Na_2HPO_4 KH_2PO_4). Further encouragement was given because the P addition also increased the leachate pH to near neutrality, the region most suitable for CH_4 production. The buffering of acidic pH's is not uncommon in soils but the addition of P is. It was justified however, by the need to detect methanogenic activity in the soil within a reasonable time. After P addition, the leachate was diluted to yield a COD = 5700 mg/ℓ to be more representative of in situ leachates (7,8).

Prior to the column experiments two completely mixed reactors (CMR) were operated anaerobically with daily additions of the leachate described above. After four weeks, methane production had been established with substantial COD reduction. The biological culture so developed was used to seed the soil/columns uniformly with depth at a level of 50 mg/ℓ as volatile suspended solids (VSS). This was designed to reduce lag time for methanogenic culture development in the columns.

Leachate was added to the columns at a Darcy velocity (q) of 1.54 cm/day. Measurements of COD, TOD, Cl, P, pH, nitrogen (N) and gas production were performed on the column influents and effluents to assess microbial activity.

RESULTS

The results obtained from the parallel column experiments are presented below.

Hydraulic Properties of Columns

Figure 2 shows the normalized tracer output curve for column R-2. The data points represent the response to a step function addition of Cl introduced on the 90th day of operation with $q = 1.54$ cm/day. The curve is typical of saturated flow through porous media.

A least squares analysis was used to fit the equation

$$n \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(n D_x \frac{\partial C}{\partial x}\right) - q \frac{\partial C}{\partial x} \qquad 1.$$

where: n = porosity
x = axial flow direction, (L)
D_x = dispersion coefficient in the x direction, $(L^2 t^{-1})$
v = interstitial velocity, $(L t^{-1})$
$q = nv$ = Darcy velocity, $(L t^{-1})$
C = tracer concentration, $(M L^{-3})$

to the tracer data. The fit achieved is represented by the solid curve for which the values of v, D_x and n are shown. The fitted value of D_x is less than the predicted by the equation of Van Genuchten and Wierenga (13);

$$D_x = 4v \qquad 2.$$

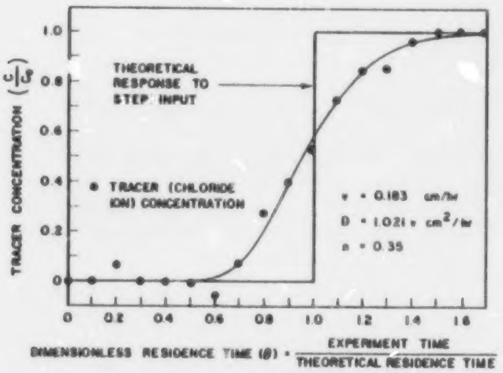

FIGURE 2

TRACER BREAKTHROUGH CURVE

Organic Matter Destruction

Figure 3 shows the concentrations of COD and TOC in the effluent from Columns R-2 and R-3 under conditions of parallel operation. While the data are somewhat scattered, they show that the removal of organic matter in the columns increased from nil initially to near 90% after 70 days of operation. This was considered to be excellent removal across a soil column distance of 41 cm. In spite of the column having been seeded with 50 mg/ℓ VSS, a lag of approximately 10 days was experienced prior to the initiation of CH_4 production. This is not uncommon for microorganisms placed in new environments. An analysis of gas production and COD removal showed that the initial active microbial population $(X(t=10,x))$ was approximately 20 mg/ℓ VSS. This indicated that some microorganisms had died off or become inactive during the lag period.

After column R-3 was taken out of service, attempts were made to measure the concentration of microorganisms within the soil. The soil was removed in sections and analysed immediately for VSS. However, the data from these measurements were too scattered to permit interpretation.

Gas Production

The data shown in Figures 4 and 5 show the production of gaseous carbon as methane (CH_4-C) and carbon dioxide (CO_2-C) in the soil columns. The scatter in the data was attributed to flow variations and to the movement of gas up through the soil prior to release. The production of CH_4 lagged behind CO_2 production initially but increased to a maximum rate after 70 days. At this time the volumetric gas composition was 19% CO_2 and 81% CH_4.

A carbon balance performed on column R-2 using averaged values for days 60 through 80 inclusive is presented in Table 4. Total carbon (TC) input to the column was measured at 221 mg/day. The TC output was composed of carbon in solution in the effluent = 62 mg/day, TC in the gases produced = 137 mg/day and TC incorporated into new microbial cells synthesized = 8 mg/day for a total of 207 mg/day or 94% recovery. The TC incorporated into new cells was calculated from estimates of cell yield and cell composition.

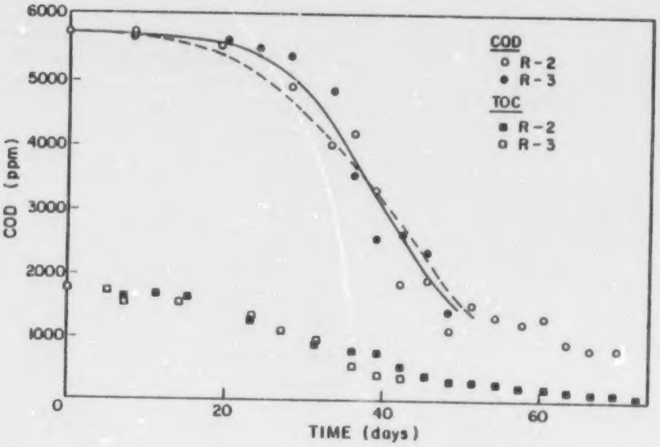

FIGURE 3

EFFLUENT COD AND TOC CONCENTRATIONS FOR R-2 AND R-3

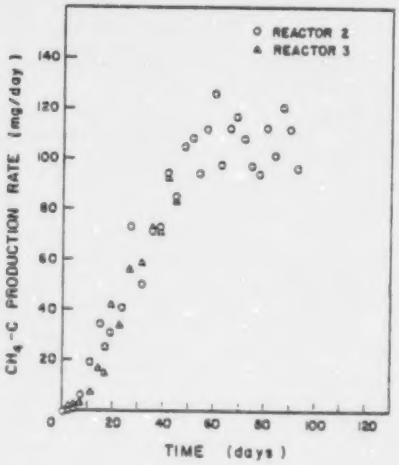

FIGURE 4

CH_4 PRODUCTION

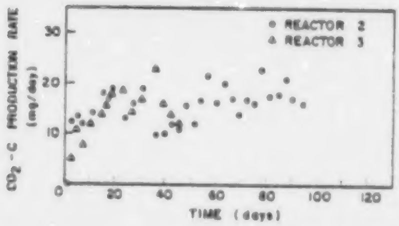

FIGURE 5

CO_2 PRODUCTION

TABLE 4

CARBON BALANCE IN COLUMN
(60th - 80th day means)

CARBON IN
1. liquid in
TOC = 210 mg/day
IC = 11 mg/day
TC (IN) = 221 mg/day

CARBON OUT
1. liquid out
TOC = 18 mg/day
IC = 44 mg/day
TC = 62 mg/day
2. gas out*
CH_4 = 119 mg/day
CO_2 = 18 mg/day
TC = 137 mg/day
3. cell synthesis
cell TC = 8 mg/day
TC (OUT) = 207 mg/day
(94% recovery)

* volumetric ratio, $CO_2 : CH_4 = 19 : 81$

Model Development

The reduction of organic matter expressed as COD was represented by Monod-type equations given as

$$\frac{dS}{dt} = \frac{kSX}{K_s+S} \qquad 3.$$

$$\frac{dX}{dt} = \frac{YkSX}{K_s+S} - b\,X \qquad 4.$$

where:
- S = substrate concentration as COD, (ML^{-3})
- X = microorganism concentration as VSS, (ML^{-3})
- k = maximum substrate utilization rate, (t^{-1})
- K_s = half velocity coefficient, (ML^{-3})
- Y = yield coefficient
- b = microbial death rate, (t^{-1})

Equation 3 was combined with Equation 1, to yield;

$$n\frac{\partial S}{\partial t} = \frac{\partial}{\partial x}\left(nD\ \frac{\partial S}{\partial x}\right) - (nv)\frac{\partial S}{\partial x} - n\left(\frac{kSX}{K_s+S}\right) \qquad 5.$$

A computer programme was assembled to solve these equations using the finite element technique presented by Sykes (14).

Suitability of the Model

The equations presented above were used to simulate the experimental results of this study. However, the parameter values chosen were based on data available elsewhere. This was done to emplore the applicability of the model in the absence of site specific experiments. The biological parameter values for k, K_s, b and Y were based on the work of O'Rourke (11) involving the anaerobic decomposition of free volatile fatty acids. The dispersion coefficient D_x was taken from the work of Van Genuchten and Wierenga (13). The parameter values used are shown in Table 5.

TABLE 5

$S(t=0, x) = 5700$ mg/ℓ
$t_{lag} = 10$ days
$X(t=10, x) = 20$ mg/ℓ

n = 0.4
v = 4.1 cm/day
D = 3v cm^2/day (Van Genuchten and Wierenga)

	(O' Rourke)
Y = 0.04	(0.04)
b = 0.015 $days^{-1}$	(0.015 $days^{-1}$)
K_s = 2800 mg/ℓ	(2 000 - 10 000 mg/ℓ)
K = 3.6 $days^{-1}$	(3.6 - 3.9 $days^{-1}$)

The values of S(0), v and n were known from the operating conditions of the column. Only the establishment of X(0) required use of the experimental results because of the microbial die-off described previously. Thus, no fitting of the equations to the data was involved. The results of this effluent COD simulation are shown as the broken line on Figure 3. Considering the use of parameters developed elsewhere, the fit is good. It supports the expectation that available information and methodology can be employed to obtain useful estimates of organic matter decomposition in soil at landfill sites.

The solid line in Figure 3 shows an improved fit after manipulation of some of the parameter values. Because of the large number of parameters in the model, manipulation must be based on an understanding of the operative physical and biological phenomenon and the use of constrained nonlinear parameter estimation techniques.

The model output tends to underpredict the experimental data as the total COD removal percentage increases. The higher than expected effluent COD values have been attributed to the presence of multiple substrates in the leachate. The model assumes a single limiting substrate reaction and thus, the use of a multiple substrate model is required.

The multiple substrate concept is supported by the fact that 54% of the leachate TOC was in the form of free volatile fatty acids. These are used readily by the methanobacteria. The balance of the organic matter would not be readily useable by the methanobacteria and hence would be converted more slowly resulting in the "tailing-off" of the effluent COD data.

Sensitivity Analysis

An analysis was performed to determine the extent to which variations in K_s and $X(t = 0, x)$ would affect COD reduction in the soil columns. The other biological parameters, particularly Y and b were held constant because they were characteristic of free volatile fatty acids (11) and not simply leachate type.

The results of the analysis are shown in Figure 6. The values for K_s lie within the range of 2000 mg/ℓ to 10,000 mg/ℓ as identified by O'Rourke (11). The variation is substantial and suggests a doubling in the time required for COD removal. A similar trend is shown for variations in $X(t = 0, x)$. In this case, the upper limit of $X(t = 0, x) = 20$ mg/ℓ VSS is the microbial concentration determined for the seeded column experiments. The lower limit is more representative of conditions which might exist leachate. It corresponds to a microbial population on the order of 10^6 cells/100 mℓ. Although no data enumerating the methanogenic bacteria in leachate are available, populations of other microbial types have been measured in excess of 10^6 cells/100 in landfill leachates (12).

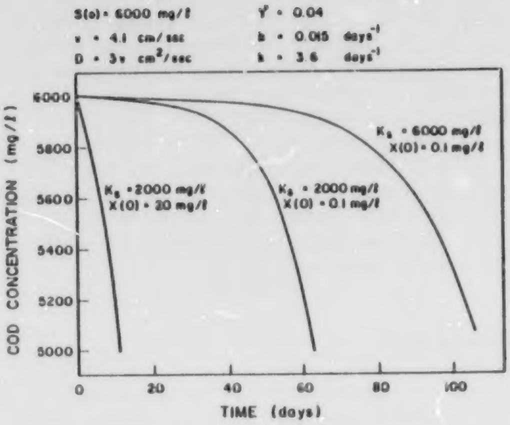

FIGURE 6

MODEL SENSITIVITY TO K_s AND X(0)

The sensitivity analysis underscores the need to ensure that the parameter values be realistic for applications of the model. It shows as well however, that even for conservative estimates of parameter values, substantial COD removal will occur within a one year period. In the context of most landfill operations, this is a significant observation.

ASSESSMENT

The scope of the work is limited and thus caution must be exercised in applying the results to new situations. Some guidelines for use are identified below.

Substrate Type

The leachate used with its acidic pH, its high volatile acid content and its P deficiency was typical of many reported elsewhere. However the organic composition of certain leachates may deviate substantially from the composition used here. In such cases an individual assessment of kinetic parameter values would be required.

An important extension of the work is the study of the microbial decomposition of organic matter present in other liquids discharged to the soil for disposal. Beyond the assessment of kinetic parameters is the search for substances inhibitory to methanogenic bacteria. Examples of inhibitory concentrations for several common ions are presented in Table 6. While such concentrations are not usually present in landfill leachates, they may be in industrial liquids to the point where CH_4 production and thus COD removal would be slowed or even halted.

P Deficiency

It has been shown that a minimum COD:P ratio is necessary for the growth of methanobacteria. Concentrations of P beyond this minimum level may serve to increase reaction rates the extent of which must be evaluated. While the addition of P to enhance microbial activity at landfills seems difficult to justify, it may not be in cases of liquid waste disposal.

Soil Properties

The most important soil properties with respect to the removal of organic matter are acid neutralizing capacity, sorptive capacity particularly for biologically resistant compounds and fluid flow related properties.

Not only does neutralization reduce acidity, it may also initiate toxic metal precipitation both of which will enhance

TABLE 6

INFLUENCE OF SEVERAL IONS ON METHANE FORMING BACTERIA

ION		CONCENTRATIONS WHICH ARE			
		Stimulatory	Inhibitory		
			Moderately	Strongly	Reference
		(mg/ℓ)	(mg/ℓ)	(mg/ℓ)	
sodium	(Na^+)	100-200	3500-5500	> 8000	(5)
potassium	(K^+)	200-400	2500-4500	>12000	(5)
calcium	(Ca^{2+})	100-200	2500-4500	> 8000	(5)
magnesium	(Mg^{2+})	75-150	1000-1500	> 3000	(5)
iron	(Fe^{3+})	20- 50	non-toxic		(5)
aluminum	(Al^{3+})	-	" "		(5)
copper	(Cu^{2+})	-	-	> 2	(15)
zinc	(Zn^{2+})	-	-	> 2	(15)
nickel	(Ni^{2+})	-	-	> 2	(15)
chromium	(Cr^{6+})	-	-	to solubility limit	(15)
ammonia	$(NH_4^+$	50-200	1500-3000	> 3000	(5))
sulphide	(S^{2-})	-	-	> 200	(16)

the growth of methane bacteria. Not all soils possess this capacity (17) and, thus, site specific measurements are required.

Although the sorption of leachate organic matter onto soil is generally poor (9,10) the sorption of specific compounds may not be. An example is the extensive sorption of the biologically resistant compounds, PCB's (18,19). Further work on sorption is required specifically with hazardous organic matter.

With respect to microbial decomposition, fluid flow is important in terms of reaction time per unit distance. As the rate of flow increases, the active microbial zone will tend to expand. However, the active zone in this study was only 41 cm to achieve 90% COD removal at a Darcy velocity of 1.54 cm/day. Thus, even a ten fold increase in the size of this active zone would not be a problem at most landfills.

Clogging of the soil due to microbial growth has been a subject of concern at landfill sites. The results of this study showed a reduction in soil permeability from 1.3×10^{-3} cm/sec initially to 1.1×10^{-3} cm/sec after 120 days of microbial activity. This was not considered to be serious, but further investigations over longer periods are required before significant conclusions can be drawn.

SUMMARY

The results of this work showed that extensive removal of leachate organic matter is possible in soil through the action of microorganisms. While further work is necessary to quantify microbial reaction parameters in response to various conditions and to provide field verifications, available information suggests that microbial decomposition in soil is active at many landfills. Since leachates tend to be acidic with much of their organic matter composed of free volatile fatty acids, it would appear that methane production occurs in the soil where pH is buffered and not in the landfill.

The microbial processes were expressed in terms of Monod-type equations to be used as a model along with expressions for advection and dispersion to simulate COD reduction in the columns. The biological parameters used in the simulation were taken from reports external to the study. Yet the quality of the simulation was good. This supported the idea that the methods and concepts presented in the study were broadly applicable to landfills and to other waste disposal systems as well. Guidelines for application to other situations were presented.

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USE OF POLLUTANT MOVEMENT PREDICTIONS TO IMPROVE SELECTION OF DISPOSAL SITES*

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ABSTRACT

The characteristics of soils in restricting the movement of pollutants are one factor in the selection of safe disposal sites. Improvements in the measurements and prediction of pollutant-soil interactions will allow the selection of disposal sites that are less likely to contaminate underlying waters and may promote favorable public opinion and rulings from zoning and regulatory groups; factors that significantly impact the approval of a proposed disposal site. This paper discusses the current status of two studies of pollutant movement modelling and the possible application of their results to disposal site selection. Although quantitative predictions of nonconservative pollutant movement in field soils do not appear feasible at present, it is concluded that qualitative predictions are within present capability and can improve the selection and management of disposal sites.

*Manuscript of the paper not received in time for publication.

INTERACTION OF SELECTED LINING MATERIALS WITH VARIOUS HAZARDOUS WASTES

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ABSTRACT

The results of the first year of exposure of a range of lining materials to selected hazardous wastes are presented. The lining materials under study in this ongoing experimental research project include a native soil, treated bentonite clay, soil cement, hydraulic asphaltic concrete, an asphaltic membrane, and a wide range of commercial or developmental polymeric membranes. The polymers used in the manufacture of these membranes are polyvinyl chloride, chlorinated polyethylene, chlorosulfonated polyethylene, ethylene propylene rubber, neoprene, butyl rubber, an elasticized polyolefin, and a thermoplastic polyester. The nine hazardous wastes selected for exposure testing included strong acids, strong bases, oil refinery tank bottom wastes, lead wastes from gasoline, saturated and unsaturated hydrocarbon wastes, and a pesticide.

Specimens of the linings were exposed to the wastes both by total immersion in the wastes and one-side exposure as a lining at the bottom of a cell under one foot of waste.

The effects of the wastes on the linings were measured by changes in physical properties of the lining and, in the case of the polymeric materials, by swelling. Initial results indicate highly specific reactivity of the linings with respect to the wastes. The results also indicate the importance of the specific composition of the polymeric linings.

INTRODUCTION AND OBJECTIVES

Confining and controlling hazardous wastes through the use of manmade impervious lining materials appears to be a feasible means of preventing seepage of pollutants in wastes from entering and polluting the ground water. A great range of materials, differing in permeability to water and potential wastes, composition, form and shape, and costs, have been used or are potentially useful for confining a range of pollutants (1).

The ongoing project on which this paper is based was undertaken with the following broad objectives:

1. To determine the effects of exposing a selected group of lining materials to various hazardous wastes over an extended period of time.

2. To determine the durability of and the cost effectiveness of utilizing synthetic membranes, various admix materials, and native soils as liners for hazardous wastes storage and disposal ponds.

3. To estimate the effective lives of 12 lining materials exposed to 6 types of industrial nonradioactive hazardous waste streams under conditions which simulate those encountered in holding ponds, lagoons, and landfills.

This paper presents current results of the exposure of a wide range of lining materials to 9 hazardous wastes, water, and weather. A more complete and detailed report of this work is now being prepared (2). Details regarding the experimental approach, the design and construction of the exposure cells, test methods, and preliminary test results are reported in the proceedings of the Tucson meeting (3) and in the First Interim Report (4).

EXPERIMENTAL APPROACH AND METHODOLOGY

Our basic approach in meeting the objectives is to expose specimens of the various commercial lining materials under conditions which simulate real service using actual wastes, to measure seepage through the specimens, and to measure effects of exposure by following changes in important physical properties of the respective lining materials.

In this study, various lining materials have been or are being subjected to 7 types of exposure testing:

- Bench screening tests; small specimens immersed in wastes.
- Primary exposure cells; one-side exposure to waste.
- Immersion of liners in wastes; two-side exposure.
- Weather test; roof exposure.
- Weather test; small tubs lined with membranes and containing wastes.
- Water absorption at room temperature and 70°C.
- Membrane bags containing wastes in deionized water; one-side exposure.

BENCH SCREENING TESTS

The bench screening tests were performed early in the project (3,4) to determine which combinations of lining materials and wastes should be installed in the primary cells for long-term exposure testing. It was recognized that some of the lining materials would be unsuitable for the confinement of certain wastes or that the service lives could be expected to be short. It was desired to eliminate such combinations. For these tests small specimens of the lining materials were hung or placed in contact with the wastes. Swelling and general effects of the exposure were observed.

PRIMARY EXPOSURE CELLS

The major effort of this research program is to assess the various lining materials in test cells under conditions which simulate real service. Test cells were designed to meet this requirement, as shown in Figures 1 and 2.

The version shown in Figure 1 is suitable for thin membrane materials; the version shown in Figure 2 is for thicker materials, up to 12 inches. These are the primary cells of this research project.

The lining specimens, approximately 1 foot in area, are placed in these cells under one-foot of waste. All of the specimens except the asphaltic membranes are in direct contact with the waste. The latter are covered with 2 inches of silica sand.

This design allows one-side exposure of the liner to the waste and measurement of permeation or seepage of the waste through the liner. Each combination of waste and liner was installed in duplicate in order that the samples could be exposed for two lengths of time. The liners can be retrieved and appropriate tests performed to determine the effects of the wastes as a function of time with the expectation that an estimate can be made of service life and durability of the lining materials.

IMMERSION OF LINERS IN WASTES; TWO-SIDE EXPOSURE:

In order to extend the matrix of liner/waste information, additional membrane lining specimens were hung in selected primary cells and additional wastes. This type of exposure presents two sides of the liner to the waste which should accelerate the effects of the wastes. Weight and area changes of the specimens and measurements of physical properties can be made. Furthermore, hanging specimens in the wastes can allow the various phases or layers of the wastes to come in contact with the specimens. This is in contrast to the primary cells in which the lining specimen is at the bottom of the cell and only the lower phase of the waste, probably aqueous, directly contacts the liner.

WEATHERING TESTS: ROOF EXPOSURE ON RACK AND IN SMALL LINED TUBS

As liners in actual service are often exposed to the weather, two weathering tests were included in this project. In one test small specimens are exposed on a rack on the roof and removed periodically

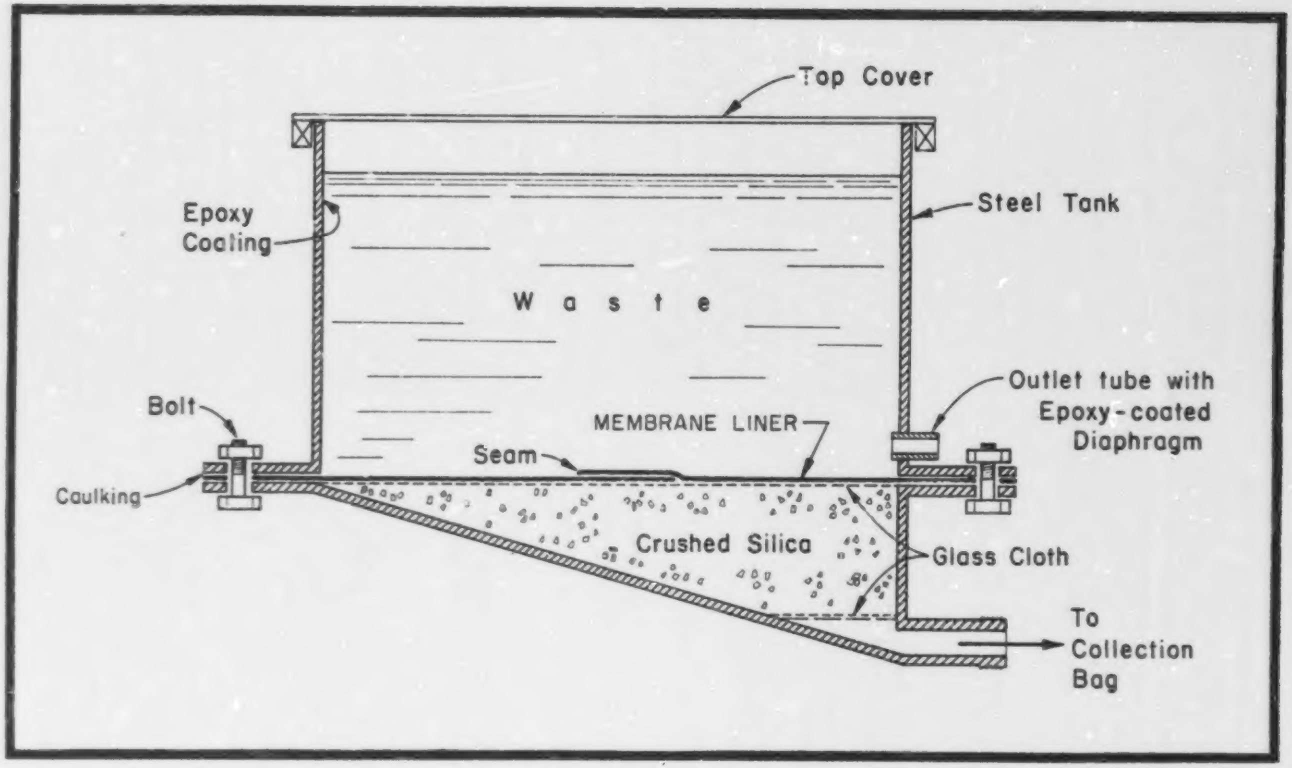
Top Cover
Steel Tank
Epoxy Coating
Waste
Outlet tube with Epoxy-coated Diaphragm
Bolt
MEMBRANE LINER
Seam
Caulking
Crushed Silica
Glass Cloth
To Collection Bag

Fig. 1 - Exposure Cell for Membrane Liners.

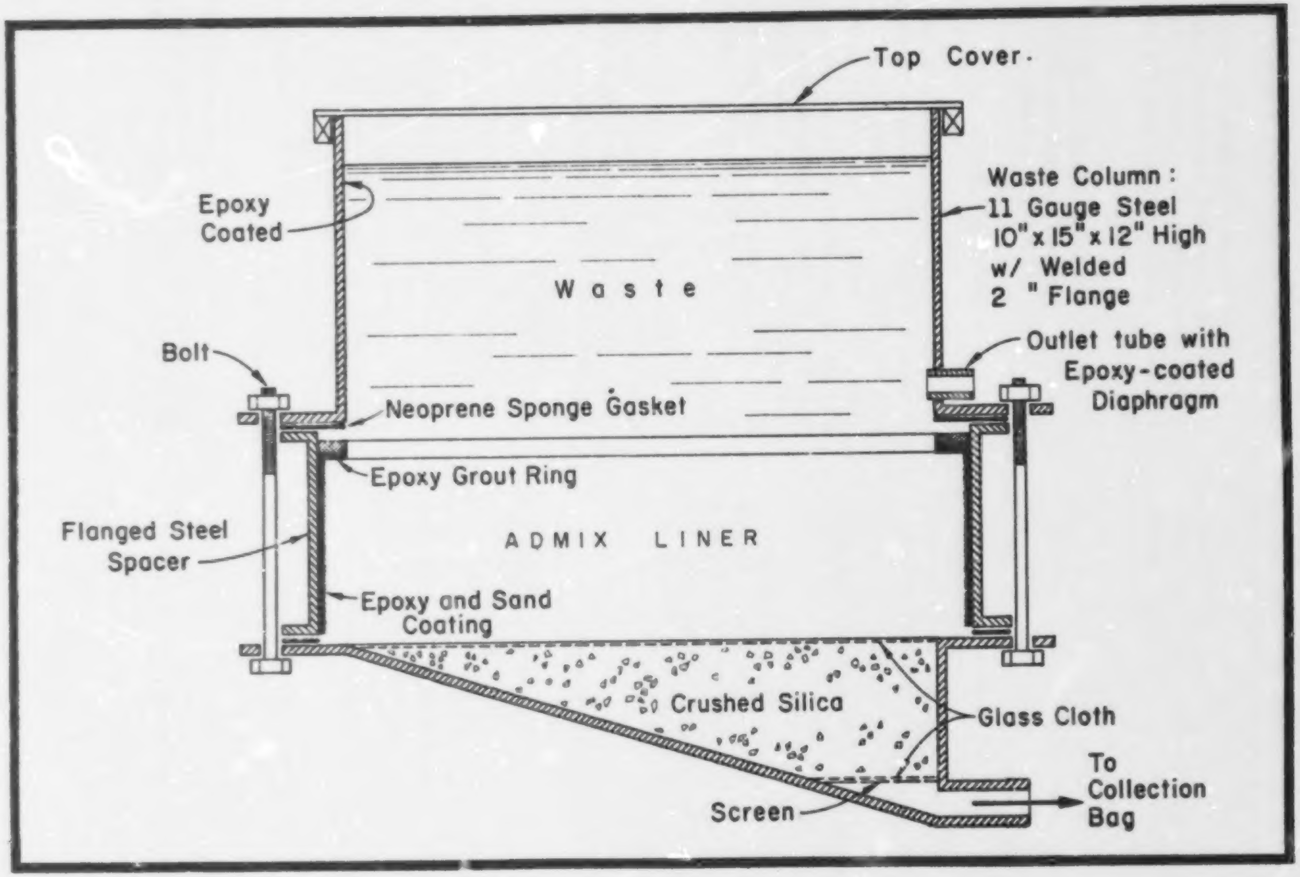
Top Cover.
Waste Column: 11 Gauge Steel 10" x 15" x 12" High w/ Welded 2 " Flange
Epoxy Coated
Waste
Outlet tube with Epoxy-coated Diaphragm
Bolt
Neoprene Sponge Gasket
Epoxy Grout Ring
Flanged Steel Spacer
ADMIX LINER
Epoxy and Sand Coating
Crushed Silica
Glass Cloth
To Collection Bag
Screen

Fig. 2 - Exposure Cell for Thick Liners.

to determine changes in dimensions, weight, and hardness. They also can be removed and their stress-strain properties determined.

In addition, 12 small plywood tubs were lined with polymeric membrane lining materials in which seams had been incorporated. These tubs were filled with the same wastes as used in the primary and immersion tests. This type of test simulates open-air service, such as in ponds, and combines the weather and waste exposure simultaneously. These tubs also feature draping of the liner over sharp corners to simulate a severe condition encountered in the field, i.e., sharp objects. Materials which are subject to ozone cracking or creep are susceptible to failure at such points. The open exposure can also result in considerable warming of the wastes in summer weather, which can accelerate deterioration.

WATER ABSORPTION AT ROOM TEMPERATURE AND 70°C

As most of the wastes contain water which can affect various polymeric lining materials, two series of exposures were undertaken, one at room temperature and the other at 70°C, the latter to accelerate water absorption.

MEMBRANE BAGS CONTAINING WASTES

In the ongoing EPA study of liners for sanitary landfills (5), a test method is being developed which was applied to the liners for hazardous wastes. In this method, small bags of heat-sealable polymeric membranes are fabricated and filled with wastes or test fluids. These bags are sealed and immersed in deionized water.

To determine the permeability of the membranes to water and pollutants, the pH and electrical conductivity of the deionized water and the change in weight of the filled bags are determined as a function of time. At the end of the exposure period, these bags are emptied and the physical properties of the liners determined. Thus, in this test, it is possible for both short and long periods of time to determine:

- The permeability of the liner to both wastes and water.

- The functioning of the seams.

- The durability of the material to one-side exposure to a waste.

This type of bag is shown in Figure 3.

DESCRIPTION OF HAZARDOUS WASTES

A total of 9 hazardous wastes from the petroleum, chemical, and pesticide industries were selected for use in this test program. They included the following basic types:

- 2 strongly acidic wastes.
- 2 strongly alkaline wastes.
- 1 lead waste (a blend of 3).
- 3 oily wastes.
- 1 pesticide waste.

Data on these wastes are presented in Tables 1 and 2. The scheme of waste analysis described by Stephens (6) has been followed in general. Six of the wastes were placed in the primary cells for exposure testing of liner materials (see Table 1). The additional 3 wastes were placed in several additional cells, but the primary purpose for these was for use in the immersion tests.

Individual wastes are briefly described below. The designation for each waste is shown in quotes, taken from the barrels in which the wastes were delivered.

Acidic Wastes

Waste "HNO_3-HF-HOAC" is a mixed acid containing nitric, acetic, and hydrofluoric acid. It was reported to contain approximately 17% nitric acid. It is a transparent, light-straw colored material containing a small amount of suspended solids and has the viscosity approximately that of water. It contains no organic fraction. This waste was used in both the primary exposure and immersion tests.

"HFL" is another relatively strong acid; however, it is far weaker than the above acid. "HFL" was used in immersion tests only.

Alkaline Wastes

"Slopwater" is basically a water solution of caustic. It has a high pH and contains a high percentage of various briny solids. This waste was used in immersion tests only.

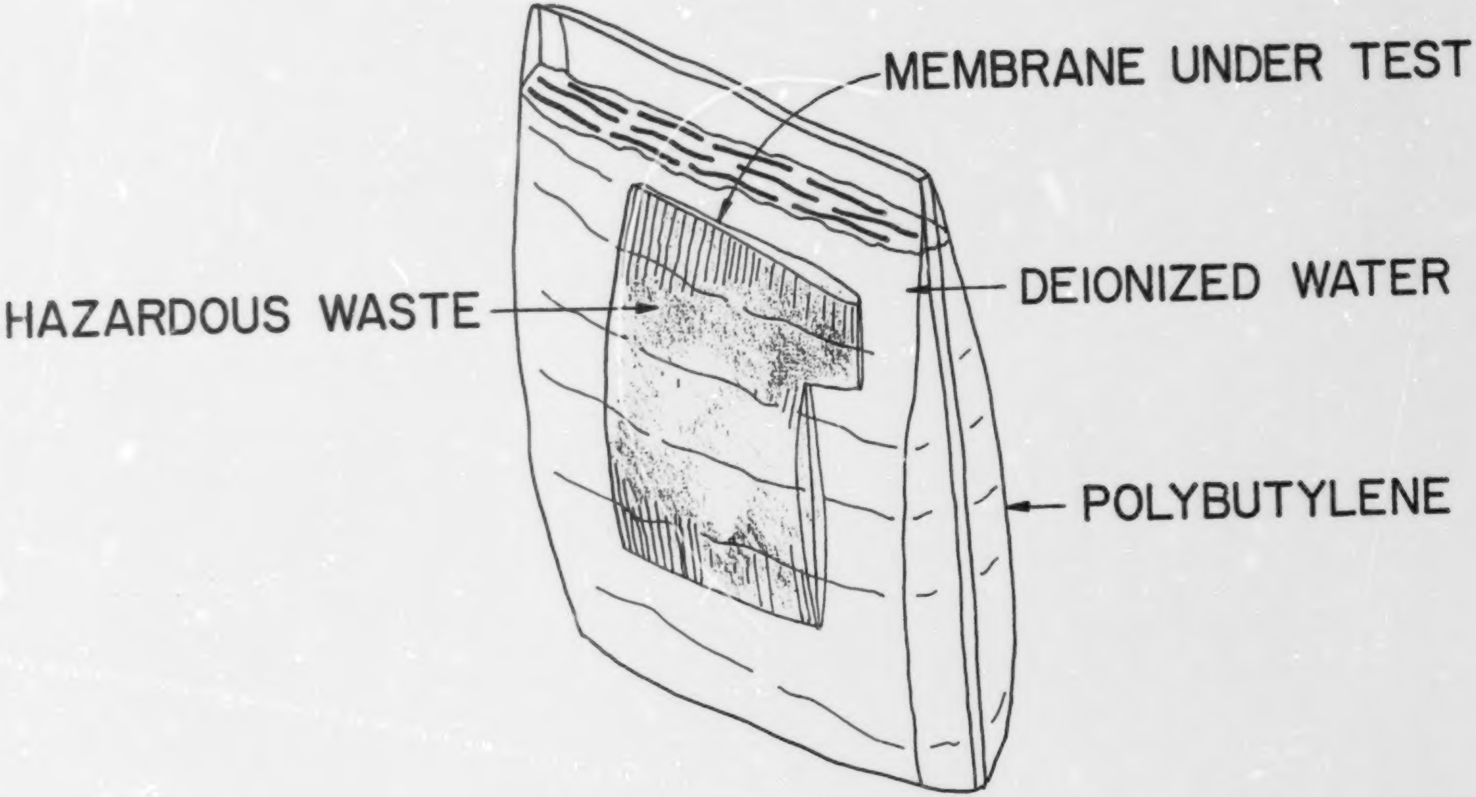
MEMBRANE UNDER TEST
HAZARDOUS WASTE
DEIONIZED WATER
POLYBUTYLENE

Fig. 3 - Bag Containing Waste Immersed in Water.

TABLE 1. WASTES IN EXPOSURE TESTS

Phases

Type of Waste	Name	Organic Phase I	Water Phase II	Solids Phase III
Acidic	"HFL"[a]	0	100	0
	"HNO_3, HF, HOAC"[b]	0	100	0
Alkaline	"Slopwater"[a]	0	100	0
	"Spent caustic"[b]	0	95.1	4.9
Lead	"Low lead gas washing"))Blend[b]	10.4	86.2	3.4
	"Gasoline washwater")	1.5?	89.1?	-
Oily	"Aromatic oil"[b]	100	0	0
	"Oil Pond 104"[b]	89.0	0	11.0
	"Weed oil"[a]	20.6	78.4	-
Pesticide	"Weed killer"[b]	0	99.5	0.5

[a] In both primary exposure and immersion tests.

[b] In immersion tests only

TABLE 2. WASTES IN EXPOSURE TESTS

pH, Solids, and Lead

Type of waste	Name	pH Water phase	Solids, %		Lead, ppm
			Total	Volatile	
Acidic	"HFL"	4.8	2.48	0.9	-
	"HNO_3, HF, HOAC"	1.5	0.77	0.12	-
Alkaline	"Slopwater"	12.0	22.43	5.09	-
	"Spent caustic"	11.3	22.07	1.61	-
Lead	"Low lead gas washing"	7.2	1.52	0.53	34
	"Gasoline washwater"	7.9	0.32	0.17	11
Oil	"Aromatic oil"	-	-	-	-
	"Oil Pond 104"	-	*ca.* 36	*ca.* 31	-
	"Weed oil"	7.5	1.81	1.00	-
Pesticide	"Weed killer"	2.7	0.78	0.46	-

"Spent caustic", obtained from the petroleum industry, is a somewhat less alkaline waste. It is transparent, tan-colored, containing white crystalline solids in suspension. It contains no oily material and has a strong soapy odor. Its viscosity is much like water; however, when cool, considerable crystallization occurred which caused problems in the mixing and pumping of this waste in the loading of the cells.

Lead Waste

Three lead wastes were originally obtained, two of which are listed in the tables and a third which had a very low-lead content and was essentially aqueous. All of the two listed, which contained most of the lead, were blended and a minor amount of the third was added to make the volume needed to fill the primary cells. This blended waste contains considerable gasoline and suspended solids. Originally this was not considered to be an oily waste, as the first samples received were aqueous, thus pointing out a problem in obtaining representative samples of wastes.

The blended waste has a low-viscosity and separates into aqueous and oily phases. Such a waste, with its low-boiling hydrocarbons and water, can be expected to cause damage to organic-type lining materials, such as the polymers and asphalts.

Oily Wastes

Aromatic oil is a highly aromatic, high-viscosity oil, such as used in the manufacture of carbon black. It is an opaque brown oil containing some suspended solids. It required heating in order to be pumped into the test cells.

"Oil Pond 104" is predominantly oil with some suspended solids. It is a naphthenic hydrocarbon and contains no water.

"Weed oil" is an oil-water mixture with a relatively low-molecular weight oil. This waste separated with the water phase on the bottom. It was used in immersion tests only.

Pesticide Waste

"Weed killer" is an herbicide, and is predominantly water with a minor amount of clay or talc as solid carrier. A waste of this type should have a minimum aggressive character with respect to linings.

SOIL AND ADMIX LINER MATERIALS

The 5 soil and admix lining materials which were selected for this test are:

	Thickness, inches
Asphalt emulsion on nonwoven fabric	0.3
Compacted native fine-grain soil	12.0
Hydraulic asphalt concrete	2.5
Modified bentonite and sand	5.0
Soil cement with seal	4.0

Linings of these materials are prepared on site. The preparation of these lining materials is described in Reference 4. These materials all have water permeabilities less than 10^{-7} cm/sec (4).

The admix lining materials are being subjected to appropriate tests from the following list before and after exposure to wastes:

Permeability
Density and voids
Water swell
Compressive strength
Penetration of asphalt
Viscosity of asphalt

All of the liners were tested initially for water permeability. The permeability of the lining material to the waste is determined by the amount of the wastes which seep through the liner. Samples can also be taken from the liner after exposure and tested for permeability to water or water vapor.

POLYMERIC MEMBRANE LINING MATERIALS

Eight polymeric membranes, based on different polymers, were selected for these exposure tests:

	Thickness, mils
Butyl rubber	34-R
Chlorinated polyethylene (CPE)	30
Chlorosulfonated polyethylene	34-R
Elasticized polyolefin	23
Ethylene propylene rubber (EPDM)	37
Neoprene	32
Polyester elastomer (developmental)	8
Polyvinyl chloride (PVC)	33

R = Fabric reinforced

All of these membrane linings, except the polyester elastomer, are commercial products. The polyester elastomer membrane, although still in development, was included because of its reportedly high resistance to oily wastes.

The physical properties which were measured on the original materials are:

*Tensile strength
*Elongation at break
*Modulus, S100 and S200
*Tear strength
Hardness
Puncture resistance
Water vapor permeability
Seam strength
Swelling in water and waste

*Tested with and across grain.

Details regarding these materials and their properties are reported in Reference 4.

After exposure to the wastes the liner materials are subjected to most of the same tests listed above. Several of the tests are being run in two directions. This is necessary because of the grain introduced in the membranes during manufacture. In most cases the data in the two directions of test are averaged for assessing the effects of exposure.

In addition to physical properties, the following analytical tests are being run on individual membrane liners to determine their basic compositions:

- Density
- Ash content
- Extractables
- Polymer content
- Carbon black content

EFFECTS ON LINING MATERIALS OF EXPOSURE TO HAZARDOUS WASTES

LINERS IN PRIMARY CELLS

Monitoring During the Exposure Period

The overall performance of the cells during the monitoring period was satisfactory for all of the cells except those containing the highly acidic waste, "HNO_3-HF-HOAC". This waste attacked the epoxy coating of the cells resulting in blistering of the coating and corrosion of the steel cell. Failure of the coating occurred primarily in the flange area at the welds, resulting in actual loss of the waste. This waste also deteriorated the polyester elastomer lining and caused failure of both of the hydraulic asphaltic concrete liners. The asphaltic concrete also leaked in one of the "spent caustic" cells and a cell containing lead waste. The cell containing the "spent caustic" was repaired and returned to exposure. The concrete liner in the cell containing the lead waste essentially lost all physical properties.

Leakage around the gasket occurred on several cells but they were repairable by tightening the bolts. Only in a couple of cases was it necessary to dismantle the cell and remount the liner.

Dismantling of Cells and Recovery and Testing of Lining Specimens

The dismantling of the cells was performed in a progressive manner, starting with the cells containing the pesticide waste and ending with the cells containing aromatic oil. This allowed the testing to be performed on specimens that had been newly removed from the cells. At the time of dismantling, the liners were photographed both in the cell and after removal from the cell. The individual liners were placed in polyethylene bags to protect them and to prevent evaporation of absorbed materials prior to testing.

All of the membrane liners and the following admix liners were removed:

- Hydraulic asphaltic concrete
- Soil cement

TABLE 3. COMBINATIONS OF ADMIX LINER MATERIALS AND HAZARDOUS WASTES

Liner Material	Thickness, inches	WASTE Acidic "HNO_3 HF-HOAC"	Alkaline "Spent caustic"	Lead	Oily Aromatic	 "Pond 104"	Pesticide "Weed-killer"
Asphalt emulsion	0.3	-	X	X	-	-	X
Compacted native soil	12.0	-	X	X	X	X	X
Hydraulic asphalt concrete	2.5	X	X	X	-	-	X
Modified clay and sand	5.0	-	-	X	X	X	X
Soil cement	4.0	-	X	X	X	X	X

- Emulsified asphalt on nonwoven fabric

All of the native soil and modified-clay sand specimens remain under exposure testing.

Admix Materials

As a result of the preliminary bench tests, specific combinations of admix liners and wastes were selected as shown in Table 3. This selection resulted in the elimination of combinations of oily wastes and the asphaltic lining materials and of acidic and highly ionic wastes and the soil and clay type linings.

The performances of the lining materials to date are described below:

Hydraulic asphalt concrete--
This lining material has given us the most difficulties. First, several of the lining specimens failed between the steel spacer and the specimen due to the difference in the coefficient of thermal expansion of steel and asphaltic concrete. This resulted in the loss of adhesion and bypassing of the liner by the waste. It was necessary to cast epoxy walls around each liner to replace the steel spacers. Second, four of the asphaltic concrete liners have leaked, two containing strong acid, one containing spent caustic, and one containing lead waste. The liners in the cells containing the strong acid failed and were removed. The liner in the cell containing spent caustic was repaired and put back in the test and the liner in the cell containing the lead waste was removed and tested.

The hydraulic asphaltic concrete liners were cored and the asphalt extracted from different layers. The asphalt in the liners from the cells containing the acid waste hardened considerably, particularly that in the top layers which were in contact with the waste (Table 4). The asphalt concrete liner from the cell containing the lead waste absorbed large amounts of the organic fraction in the waste and became very soft, almost a slush. The liner with the pesticide waste remained in satisfactory condition, retaining its compressive strength and only showing slight hardening on aging.

Emulsified Asphalt on Nonwoven Fabric--
During the leak-testing of the cells with water, considerable delamination and blistering of the asphaltic materials occurred. Consequently, two inches of silica sand was placed on these liners. As a result of the preliminary bench tests, the emulsified asphalt liner was placed only in cells containing pesticide, "spent caustic", and the lead wastes. There was no leakage in these cells during the exposure period.

The liners were recovered after 469-487 days of exposure. All appeared to be in satisfactory condition, although there was swelling of the liners taken from the cells containing lead waste and "spent caustic" waste. The relatively low swelling of this liner below the lead waste which contains volatile hydrocarbons is probably the result of the sand-water layer that was directly above the liner.

Soil Cement--
All of the wastes, except the acid waste, were placed above the soil cement

TABLE 4. HYDRAULIC ASPHALT CONCRETE AFTER EXPOSURE TO HAZARDOUS WASTES

Waste - Type	None		Acidic				Lead	Pesticide	
Name	-		"HNO_3-HF-HOAC"				-	"Weed Killer"	
Cell No.	-		C-31		C-26		C-27	C-23	
Exposure time, days	-		40		199		192	569	
HAC Concrete[a]									
Coefficient of permeability, cm sec^{-1}	1.3×10^{-8}		2.6×10^{-8}		2.4×10^{-9}		(b)	-	
Density, g/cm	2.322		-		2.294		-	2.351	
lb/ft^3	145.0		-		143.2		-	146.8	
Voids content, % vol.	4.0		-		5.8		-	3.4	
Compressive strength, psi	268		162		234		21[b]	237	
% original	-		60		87		8	88	
Extracted asphalt									
Depth from top, cm	0-1	2-3	0.3[c]-1	2-3	0-1	2-3	-	0-1	2-3
Viscosity at 25°C, MP at 0.01 s^{-1}	4.90	1.78	3.66	1.22	(d)	1.78	2.73	2.55	1.78
Shear susceptibility	0.10	0.07	0.09	0.13	-	0.14	0.11	0.03	0.14
Penetration at 25°C, calculated[e]	48	71	53	87	-	75	60	58	75

[a] Thickness of liner specimen: 6.3 cm (2.5 in.)

[b] Compressive strength measured using "Pocket Penetrometer" because cores were too soft to hold shape, so could not be tested. The gasoline absorbed from the waste evaporated along with the benzene used for extraction of the asphalt from the aggregate, so the viscosity measured does not represent the very low viscosity while the liner was in place.

[c] Asphalt from 0 to 0.3 cm was too hard to test.

[d] Asphalt from 0-1 cm was too hard to test.

[e] Calculated from absolute viscosity at 25°C.

liners. The acid waste was deleted from exposure to the soil cement because of the poor resistance of the soil to the strong acid waste as shown by the bench tests. No seepage of waste occurred through the soil cement specimens during the exposure period. On recovery, they were in satisfactory condition.

In the case of the coating on the liners exposed to the "spent caustic" and the pesticide wastes, there were some blisters. The compressive strengths of the cores taken from these liners were all satisfactory and had higher values than specimens which were not exposed to the waste but kept in polyethylene bags.

Native Soil--

All of the wastes except the acid waste were placed on the compacted soil liners. During the course of monitoring, all of the cells seeped. However, the composition of these was essentially the same in all cases, containing large amounts of salt. This soil had been dredged from the mouth of the Sacramento River and placed on land at Mare Island. It contains large amounts of salt from the water.

It is planned to dismantle these cells in the near future and to determine the migration of the wastes or their components through the soil.

Modified Clays--

Pesticide, lead waste, "Pond 104 Oil", and aromatic oil were placed on liners prepared from modified clays and sand. These clay liners were not exposed to the acid and alkaline wastes because of the failures of these materials with these wastes in the bench tests. During the monitoring there was no seepage through these lining materials. They remain under test but will be recovered within the next two months and the migration of the wastes into them will be determined.

Polymeric Membranes

The effects of the wastes upon the membrane linings can vary considerably with the polymer and the waste, as shown in Tables 5 and 6 by the elongation and hardness of the liners on exposure. Both of these properties are measures of the rubbery character of polymers. Substantial increases or decreases in either of these properties can significantly affect the performance of many rubber products. One of the objectives of this project is to determine the effects of changes in properties upon the utility of the liners. Noted on both of the tables are those combinations of liners and wastes which were not tested.

The elongation of the polyester liner in the acid waste dropped to essentially zero during the exposure resulting in the failure of this liner. The butyl liner has a low elongation because it is reinforced and breaks with the breaking of the fabric. The values shown are those at which the tensile was the maximum. In most cases, there is a drop in elongation; however, in several cases the elongation increased due to absorption of a fluid.

The hardness values generally decreased during the exposure period, particularly in those liners which were in contact with oily wastes. There were increases in hardness of the PVC liners exposed to the acid waste and to the "Pond 104" oil, probably reflecting the loss of plasticizer.

Immersion Tests of Polymeric Membrane Liners

In the immersion testing, 12 membrane liners were exposed to 9 wastes. The 6

TABLE 5. RETENTION OF BREAKING ELONGATION OF POLYMERIC MEMBRANES ON EXPOSURE TO WASTES IN PRIMARY CELLS

Polymer	Liner No.	Original Value, %	WASTE					
			Acidic	Alkaline	Lead	Oily		Pesticide
			"HNO_3 HF-HOAC"	"Spent caustic"		Aromatic	"Pond 104"	"Weed-killer"
Butyl	57-R	45	56[a]	56[a]	111	No X[b]	No X	133
Chlorinated polyethylene	77	410	88	105	100	No X	96	99
Chlorosulfonated polyethylene	6-R	245	90	69	106	No X	102	110
Elasticized polyolefin	36	665	99	100	93	96	86	101
Ethylene propylene rubber	26	470	94	98	96	No X	No X	96
Neoprene	43	320	No X	99	77	No X	86	94
Polyester elastomer	75	575	0.4[c]	104	98	77	95	96
Polyvinyl chloride	59	375	83	103	96	91	85	101

[a] Elongation at maximum tensile with failure of the reinforcing fabric.

[b] No X - No exposure test because of poor performance in bench tests.

[c] Failed at 323 days.

R = Fabric reinforced.

TABLE 6. CHANGES IN HARDNESS[a] OF POLYMERIC MEMBRANES ON EXPOSURE TO WASTES IN PRIMARY CELLS

Polymer	Liner No.	Original Value, %	WASTE					
			Acidic "HNO_3 HF-HOAc"	Alkaline "Spent caustic"	Lead	Oily		Pest-icide "Weed-killer"
						Aro-matic	"Pond 104"	
Butyl	57-R	71	-4	-2	-4	No X[b]	No X	-4
Chlorinated polyethylene	77	84	-12	-9	-17	No X	-34	-7
Chlorosulfonated polyethylene	6-R	77	-3	-2	-11	No X	-32	-4
Elasticized polyolefin	36	87	-3	-2	0	-10	-16	+1
Ethylene propylene rubber	26	58	-8	-2	-1	No X	No X	-5
Neoprene	43	57	No X	+1	-17	No X	-20	-9
Polyester elastomer	75	93	-15.5[c]	-2	-3	-10	-10	-1
Polyvinyl chloride	59	72	+12	-1	-3	-4	+4	-2

[a] Duro A - 10 sec. reading.

[b] No X - No exposure test because of poor performance in bench tests.

[c] Failed in 323 days.

R = Fabric reinforced.

basic polymers are included in the 12. However, the 12 now include 2 chlorosulfonated polyethylene, 2 ethylene propylene rubber, and 3 polyvinyl chloride membrane linings. The original 6 wastes used in the primary cells are again used in this test, plus the following:

Acidic waste - "HFL"
Alkaline waste - "Slopwater"
Oily waste - "Weed Oil"

The effect of the immersion upon the liners is shown in Table 7, which presents the increase in weight during the exposure

TABLE 7. SWELLING OF MEMBRANE LINING MATERIALS ON IMMERSION IN WASTES

% Weight increase

Polymer	Liner No.	Vulcan-ized	Acidic Wastes		Alkaline Wastes		Lead Waste	Oily Wastes			Pest-icide
			HF	HNO_3	Slop-water	Spent caustic		Aro-matic	Pond 104	Weed	Herb-icide
Immersion time, days	-	-	250	193	193	238	236	257	248	252	242
Butyl rubber	44	Yes	2.7	1.4	2.0	0.4	20.1	32.3	96.5	70.8	0.8
Chlorinated polyethylene	77	No	9.4	9.3	1.5	0.6	70.9	59.5	31.6	116.7	9.6
Chlorosulfonated polyethylene	6-R	No	6.8	10.3	3.8	3.3	83.0	51.1	75.1	202.3	13.1
	55	No	5.4	7.5	3.8	2.2	69.6	53.2	58.4	210.5	12.3
Elasticized polyolefin	36	No	0.3	2.7	17.3	0.5	18.2	21.3	33.5	44.2	0
Ethylene propylene rubber	83	Yes	3.1	2.6	2.[illegible]	1.3	23.0	15.8	35.4	73.4	3.7
	91	?	16.1	18.3	3.1	0.2	29.3	35.3	80.1	79.4	8.1
Neoprene	90	Yes	9.6	10.9	0.4	0.8	45.6	60.7	25.8	94.8	8.5
Polyester elastomer	75	No	0.6	4.2	35.1	0.6	7.6	17.1	7.9	16.3	2.4
Polyvinyl chloride	11	No	10.2	16.8	13.5	0.1	4.4	10.7	-7.7	10.0	4.0
	59	No	2.8	-2.8	-6.4	-3.0	8.8	11.3	-1.5	33.4	0.5
	88	No	7.6	19.8	-13.5	0.1	2.2	7.2	-10.3	18.1	2.9

R = Reinforced

TABLE 8. RETENTION OF TENSILE STRENGTH OF MEMBRANE LINER MATERIALS ON IMMERSION IN "WEED OIL"[a]

(Percent of original value)

Polymer	Liner No.	Original Value, psi	Retention, % Top of specimen	Retention, % Bottom of specimen
Butyl rubber	44	1520	16	55
Chlorinated polyethylene	77	2235	(b)	4
Chlorosulfonated polyethylene	6-R	1730	7	43
	55	1715	(b)	45
Elasticized polyolefin	36	2595	26	32
Ethylene propylene rubber	83	970	(b)	39
	91	1865	30	40
Neoprene	90	1940	18	32
Polyester elastomer	75	6770	90	81
Polyvinyl chloride	11	2955	72	84
	59	2555	50	42
	88	3155	63	68

[a] Immersion time, 252 days.
[b] Too soft to test.
R = Fabric reinforced.

period. As in the primary cells, the effects vary considerably with liner type and waste. In addition, there is a significant variation in the effects between materials of the same polymer. This is particularly true among the three PVC lining materials.

The hanging of the samples in the wastes allows the various phases of the waste to contact the specimens. The effect upon properties of the top and bottom sections of the test specimen is shown in Table 8.

ROOF EXPOSURE

Eleven samples of polymeric membrane liners were exposed 343 days on the roof of our laboratory in Oakland, California. They were removed, cleaned, weighed, measured, and stress-strain properties determined. Results of the liner tests are presented in Table 9. Most of these materials show a loss in elongation and an increase in modulus. The liner material which showed the greatest change was the chlorosulfonated polyethylene, which retained 61% of its elongation and doubled in modulus. This probably reflects a crosslinking of the polymer during exposure.

WATER ABSORPTION OF POLYMERIC LINERS

Results of the water absorption tests run on the same 11 polymeric membrane liners at room temperature and at 70°C are presented in Table 10. The immersion time in this experiment was 308 days. These results show the great difference in ultimate swelling of these lining materials by water. Of particular interest is the low water swell of the elasticized polyolefin membrane and of these polyvinyl chloride membranes at room temperature.

TABLE 9. RETENTION OF PROPERTIES ON ROOF EXPOSURE[a] OF POLYMERIC MEMBRANE LINING MATERIALS

(Retention in percent)

Polymer	Liner No.	Elongation at break	S-100 Modulus
Butyl rubber	57-R	125	-
Chlorinated polyethylene	77	103	116
Chlorosulfonated polyethylene	6-R	61	200
Elasticized polyolefin	36	96	117
Ethylene propylene rubber	8	93	137
	26	87	111
Neoprene	43	76	146
	82	85	107
Polyester elastomer	75	89	104
Polyvinyl chloride	11	111	105
	59	96	111

[a] 343 days in Oakland, CA.

R = Fabric reinforced.

TABLE 10. SWELLING OF POLYMERIC MEMBRANE LINERS IN WATER

(Percent weight increase)

Polymer	Liner No.	Room Temp.	70°C
Butyl rubber	57-R	4.5	53.9
Chlorinated polyethylene	77	10.2	140.0
Chlorosulfonated polyethylene	6-R	10.9	245.6
Elasticized polyolefin	36	0	0.6
Ethylene propylene rubber	8	1.6	10.8
	26	1.5	11.2
Neoprene	43	27.8	240.0
	82	18.5	191.4
Polyester elastomer	75	10.2	140.0
Polyvinyl chloride	10	0.7	39.2
	59	2.4	24.0

R = Fabric reinforced.
Immersion time: 308 days

TABLE 11. SEALED BAGS CONTAINING STRONG ACID WASTE IMMERSED IN DEIONIZED WATER[a]

Polymer	Liner No.	Deionized water		Increase in weight of bag containing waste, g.
		pH	Conductivity µ mho	
Chlorinated polyethylene	86	4.0	132	6.1
Chlorosulfonated polyethylene	85	7.7	306	8.9
Elasticized polyolefin	36	5.9	25	0.5
Polybutylene	98	3.1	296	0.6
Polyvinyl chloride	19	2.5	1970	5.0
	88	2.4	2285	11.3
Blank	-	4.9	7	-

[a] Immersion time, 337 days.

MEMBRANE BAGS CONTAINING WASTES

In this test of the liner membranes run up to 337 days, the membranes have been found to be very impermeable. There has been a slight increase in the conductivity of the deionized water outside the bags indicating some ions pass through the membranes. On the other hand, the bags have generally increased in weight, indicating the movement of water into the bags due to osmotic pressure. This is illustrated in Table 11 for the bags containing strong acid.

DISCUSSION

Although the results must be considered preliminary at this point in the exposure testing, it is quite apparent that some of the hazardous wastes can seriously affect the physical properties of lining materials. There is a highly specific interaction between lining materials and wastes which requires testing of specific liner and waste combinations for compatibility.

In characterizing the wastes, components which are aggressive toward linings should be identified. Organic constituents tend to have solvent effects upon the organic polymeric membranes and asphaltic materials. The effects will depend upon the specific components and the liner material. The acidity and ion concentration are particularly important when soils and clays are being considered.

The fact that many of the wastes are heterogeneous and can separate into oily and aqueous phases poses additional problems in the selection of lining materials. At the present time no one lining material is satisfactory for both of these components of the wastes, although some of the liners achieve a better compromise than others.

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THE USE OF LINER MATERIALS FOR SELECTED FGD WASTE PONDS

By

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ABSTRACT

A comparison was made of the compatibility of 18 linear materials and two selected FGD waste sludges. A total of 72 special test cells was constructed to contain the liners and the sludges. Devices were installed to collect leachate from the sludge, and the cells were pressurized to simulate a 30-ft head of sludge. Physical and chemical tests were conducted prior to initiating the investigation, at the midpoint (12 months) and then scheduled for the end (24 months). The leachate collected for the 12 months has been analyzed for content of approximately 20 heavy metals. Also, observations and physical tests were made of the liner materials. At the midpoint of the investigation, two of the admix liner materials had disintegrated due to reaction with the FGD sludge. The leachate analysis from the majority of the other test cells indicated a considerable attenuation of the concentration of heavy metal content as compared with the analysis of the original or raw sludge. Further tests are scheduled during the remainder of the investigation to determine the cause of this phenomenon.

INTRODUCTION

The utilization of liners for water storage ponds, irrigation canals, and even industrial waste ponds is not a new concept. There is, however, a lack of knowledge concerning the compatibility of liner materials subjected to certain toxic wastes and the life expectancy of the liners.

The U. S. Army Engineer Waterways Experiment Station (WES) has been engaged for a number of years in research of the chemical and mechanical stabilization of soils and the development of prefabricated membrane surfacings and dust control materials for military applications. On the basis of the capabilities established and procedures and materials developed by the above-mentioned research, the WES has undertaken, through an interagency agreement with the U. S. Environmental Protection Agency, a study to assess the potential feasibility for application of selected materials to use as liners for flue gas desulfurization (FGD) waste areas.

OBJECTIVES

The objectives of the study are as follows:

- a. To determine the compatibility of liner materials with FGD sludge wastes and associated liquors and leachates.
- b. To estimate the length of life for the liners.
- c. To assess the economics involved with the purchase and placement (to include construction) of various liner materials.

A subsequent objective required that the liner materials be subjected to a simulated 30-ft head (depth) of sludge, as would be expected in prototype storage ponds.

SCOPE

This paper presents the liner materials and sludge wastes selected for the study, the test devices and procedures developed, and a comparison of selected results obtained at the initiation and at the end of a 12-month period of study.

APPROACH

To accomplish the objectives, primary consideration was placed on the use of admixed and/or stabilized in situ materials; secondly, on spray-on materials; and finally, limited use of prefabricated membrane-type materials. This resulted in a requirement to study a total of 18 liner materials consisting of two prefabricated membranes, six spray-ons, and ten admix-type liners. The liner materials were subjected to two FGD sludges. The liners were installed in exposure cells designed to simulate a 30-ft depth of sludge, which was applied over a 10-month period of time for this particular study. The liner materials were scheduled to be exposed to the sludges for 12- and 24-month periods. Prior to installation in the exposure cells, physical tests were conducted on the liner materials and a chemical analysis was made of the sludges. The physical tests were scheduled to be made on the liner materials at the end of the 12- and 24-month periods of exposure. The exposure cells were so designed that any leakage of the liquid from the sludge was collected and chemical analysis of such leachate was made as required, i.e., when sufficient liquid was collected for the required analysis. The chemical analyses of the raw sludge, both solid and liquid portions, were evaluated for the presence of heavy metals, which now number 20 such parameters.

MATERIALS AND METHODS

Liners.--The selection of the liner materials involved a screening process based on prior experience with the materials and additional evaluation primarily using a test for permeability of the liner. The test for permeability was readily applicable for the membrane and spray-on materials but was modified to some extent for the admixed materials. The modification consisted of conducting the permeability test on admixed samples constructed in a Harvard miniature test apparatus. This procedure precluded construction of rather large samples and thus reduced the time and materials needed for the tests. It further provided additional samples for physical tests. Since a rather large number of admixed samples were discarded because of high permeability, new mixes were prepared with different percentages of additives. The prior research conducted at the WES for stabilization of soils required principally an increase in strength, and permeability was not considered of great importance.

The final items selected for the two prefabricated membrane liners are listed in Figure 1. Although there are hundreds commercially produced, these membranes were selected due to ease of placement and strength, which would possibly prevent damage during construction.

The spray-on materials selected for the study are listed in Figure 2. The materials are basically products of research at the WES for dust control palliatives and are the items that exhibited the greater performance potential.

The admix liner materials are shown in Figure 3. The materials (additives) are, except for the Takenaka Aqua-Reactive Chemical Soil Stabilization System (TACSS) materials, generally those commonly used for stabilization and paving purposes and for which primary consideration was for cost and ease of placement. The TACSS materials are relatively new to the United States but are reported to have been extensively used in Japan and some European countries. The materials were supplied by the parent firm, which also provided personnel to aid in preparation of the admixes. The types 020 and 025 are two-component liquids, while the C400 and ST are medium gray powders.

FGD Sludges.--The FGD sludges selected for the study consisted of one from an eastern coal lime scrubbed process and the other from an eastern coal limestone scrubbed process. The sludges were considered to be representative of what could be expected from most areas. Also, the two sludge materials are included in a study of chemical fixation of hazardous wastes being conducted by the Environmental Effects Laboratory (EEL), WES. This provided the possibility that supporting of additional

MATERIAL	TYPE	MANUFACTURER
TOTAL LINER	ELASTICIZED POLYOLEFIN (30 MIL)	THE GOODYEAR TIRE AND RUBBER COMPANY
T-16	BLACK NEOPRENE-COATED NYLON-REINFORCED FABRIC	REEVES BROTHERS, INC.

FIGURE 1. PREFABRICATED MEMBRANCE LINER MATERIALS

MATERIAL	TYPE	MANUFACTURER
DCA-1295	POLYVINYL ACETATE	UNION CARBIDE
DYNATECH FORMULATION 267	NATURAL RUBBER LATEX	DYNATECH R&D CO.
UNIROYAL	NATURAL LATEX	UNIROYAL, INC.
AEROSPRAY 70	POLYVINYL ACETATE	AMERICAN CYANAMID
AC 40	ASPHALT CEMENT	GLOBE ASPHALT
SUCOAT	MOLTEN SULPHUR	CHEVRON CHEMICAL CO.

FIGURE 2. SPRAY-ON LINER MATERIALS

MATERIAL	TYPE/PERCENT	MANUFACTURER
CEMENT	10%	DUNDEE CEMENT CO.
LIME	10%	WILLIAMS LIME CO.
CEMENT WITH LIME	4% PORTLAND CEMENT, 6% LIME	
M179	POLYMER BENTONITE BLEND 4%	DOWELL DIVISION OF DOW CHEMICAL
GUARTEC (UF)	A LIGHT GRAY POWDER 4%	GENERAL MILLS
ASPHALTIC CONCRETE	11% ASPHALTIC CEMENT, 1/2-IN. AGGREGATE	LOCAL CONTRACTORS
TACSS 020	6%	TAKENAKA CO. (JAPAN)
TACSS 025	6%	DISTRIBUTED IN U. S.
TACSS C400	15%	BY AIR FRAME MFG. CO.
TACSS ST	15%	CALIFORNIA

FIGURE 3. ADMIX LINER MATERIALS

information could be obtained from the chemical fixation study.

Chemical Properties.--The chemical properties of the raw sludges and subsequent leachates were determined for the parameters presented in Figure 4. The list basically follows the parameters being evaluated by EEL for the chemical fixation study. The chemical analysis performed was at the level of sensitivity of that obtainable by the flame AA spectrophotometry technique.

PARAMETER	PARAMETER
ARSENIC (As)	LEAD (Pb)
BERYLLIUM (Be)	SELENIUM (Se)
CADMIUM (Cd)	ZINC (Zn)
CHROMIUM (Cr)	SULFITE (SO_3)
CYANIDE (CN)	SULFATE (SO_4)
COPPER (CU)	BORON (B)
MERCURY (Hg)	CHLORIDE (Cl)
MAGNESIUM (Mg)	VANADIUM (V)
MANGANESE (Mn)	NITRITE (NO_2)
NICKEL (Ni)	NITRATE (NO_3)

FIGURE 4. CHEMICAL PROPERTIES EVALUATED FOR RAW SLUDGES AND LEACHATES

Test Cells.--The test cell developed for exposure of the liner materials to the FGD sludge is shown in Figure 5. The cylindrical portion is common PVC pipe with a wall thickness of 0.375 in. (0.953 cm) and an ID of 11.813 in. (30.004 cm). Flanges 1 in. (2.54 cm) thick were fixed to the top and bottom of the cylinder. The base, also PVC, is 2.125 in. (5.398 cm) thick and 15 in. (38.1 cm) square. The base is tapped at the center to accommodate the drain port, and a special recess provided to house a 6 in. (15.24 cm) in diameter and 0.25-in. (0.635-cm) thick porous plastic filter. The top, also, PVC, is 15 in. (38.1 cm) in diameter and 0.75 in. (1.905 cm) thick with a tap provided for pressure attachments. The top, flanges, and base are drilled to accommodate 0.375-in. (0.953-cm) bolts for connection purposes. An assembled test cell is shown in Figure 6.

The cells were pressurized through the top cover by compressed air, passing through a system of regulators, gages, and

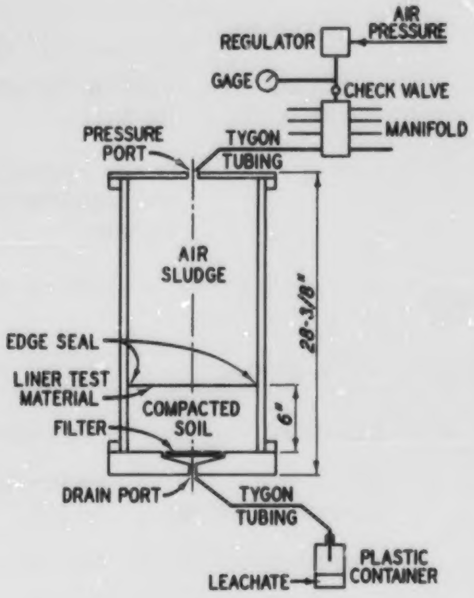

AIR PRESSURE
REGULATOR
GAGE
CHECK VALVE
MANIFOLD
PRESSURE PORT
TYGON TUBING
AIR
SLUDGE
28-3/8"
EDGE SEAL
LINER TEST MATERIAL
COMPACTED SOIL
6"
FILTER
DRAIN PORT
TYGON TUBING
PLASTIC CONTAINER
LEACHATE

FIGURE 5. TYPICAL TEST DIAGRAM

FIGURE 6. TYPICAL ASSEMBLED TEST CELL

check valves, and by a manifold to simulate the desired depth of sludge. The bottom drain port was connected to a plastic container for holding the leachate.

TEST PROCEDURES

The methods for constructing pond liners for field installations were the primary consideration in developing test procedures for the study. In this respect, the soil types encountered would be of major importance; therefore, the inclusion of soil material to be used in conjunction with the liners was a necessary measure.

The soil used with the membrane and spray-on liners and the asphaltic concrete was a nonplastic silty sand with good drainage characteristics. However, the soil used for the admix liners was a slightly plastic clayey silt, which was readily adaptable for chemical stabilization. Both soil types were locally available but widespread in occurrence and are considered representative of materials that would be encountered at disposal sites.

The sequence of constructing the test (exposure) cells consisted of assembly of the base plate and cylindrical part of the cell. Next, a silicone sealant was applied at the interface of the two parts, and the connecting bolts were secured. The filter was then placed in the recess.

The admix liners were prepared based on previously determined optimum mixtures (Figure 3). The material was placed in the cell and compacted to a thickness of 6 in. (15.24 cm). The thickness was considered to be the minimum that construction equipment would normally be capable of placing in a field installation. The exception for an admix liner was the asphaltic concrete that was premolded to a 2-in. (5.08-cm) thickness and supported by 4 in. (10.16 cm) of silty sand previously compacted at optimum moisture and density.

The silty sand that was used as a base for the membrane and spray-on liners was compacted at optimum moisture and density in the cells to a depth of 6 in. (15.24 cm). The membranes were prepared with a seam or joint along the middle of the specimen, cut to fit snugly in the cylinder, and placed on the sand base. The spray-on materials were measured to provide a placement rate of 0.75 gal/yd^2 (3.4 ℓ/m^2), poured over the sand base, and smoothed to provide a uniform thickness. The materials were then allowed to cure for the required time period.

Following installation of the liners, a silicone sealant, GE 1200, and primer, No. 3154, were applied around the periphery of the liner and on the cell wall. The result was a triangular-shaped seal that extended approximately 1 in. (2.54 cm) out on the liner and also up on the cell wall. The sealant was then allowed to cure for the required time.

The FGD sludge was thoroughly mixed until a liquid state was attained. Approximately 4 gal (15.1 ℓ) of sludge was placed in each cell.

The tops were placed on the cells for which the silicone sealant was again used at the interface with the cylinder and secured with bolts. The cells were placed on shelves in an area provided with constant temperature and humidity (Figure 7).

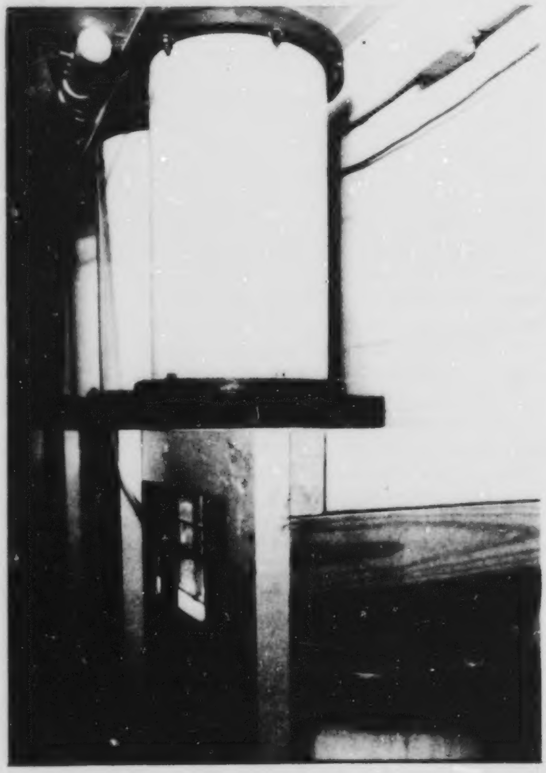


FIGURE 7. TEST CELL HOLDING AREA

The appurtenant equipment for leachate collection and pressurization was connected to complete the assembly.

A total of 72 test cells were assembled. This provided 36 cells with the two FGD sludges and 18 liner materials with each sludge for a 12-month exposure period and the remaining 36 cells for 24-month exposure.

RESULTS

The study plan required that physical tests be conducted on liner material specimens prior to their exposure, and a chemical analysis be made of the raw sludges.

The 36 cells designated for the 12-month exposure period were dismantled. Then similar physical tests were conducted, and observations made of the liner materials. Also, chemical analyses were made for the leachates collected during the 12-month exposure period. The results presented herein will, of necessity, be limited to selected data and observations because of the massive amount of data collected.

As the cells were dismantled, it was readily apparent that the solids in the sludge had settled and separated from the liquid portion. The solids were black in color and had caused discoloration of the liner surface in most of the cells. Since the solids were extremely difficult to remove from the cell, considerable caution was observed to prevent damage to the liner materials. In some of the cells, failure of the interior seal, even though minute, had occurred and allowed complete discharge of the liquid portion of the sludges. The admix materials in which M179 and Guartec had been used as additives were almost completely disintegrated. The reason for the disintegration has not yet been determined, but it is assumed to be the result of a chemical reaction of the additives with the sludges.

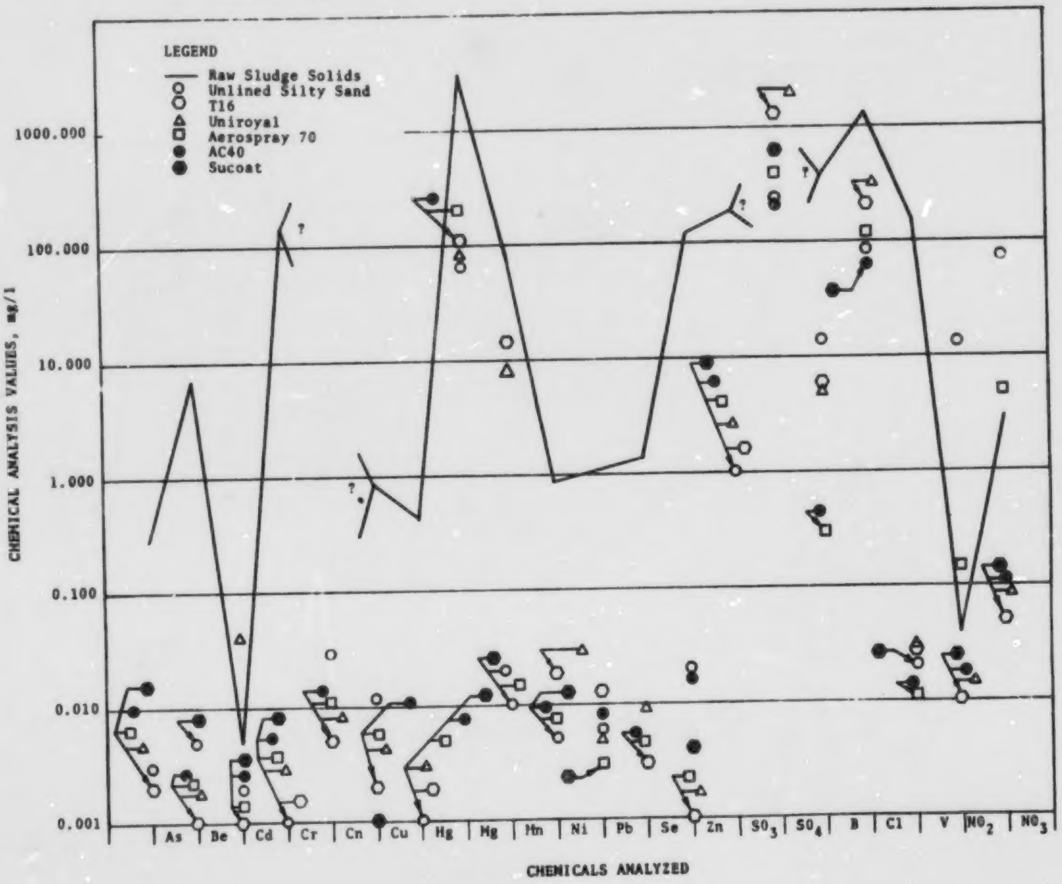
The data considered to be the most pertinent and meaningful at this stage of the study were the chemical analyses of the collected leachate as compared with that of the raw sludge, especially the solid portion. It was recognized as the study progressed that the concentration of the heavy metals in the collected leachate attenuated considerably, usually by several orders of magnitude as compared with the raw sludge solids. However, the concentrations determined for the liquid portion of the raw sludge were approximately equal to that of the leachate.

In an effort to determine the cause of such attenuation, two cells were assembled containing 6 in. (15.24 cm) of compacted silty sand without any type of liner. Sludge was added, one type in one cell and one in the other, and leachate collected as for the lined cells. A chemical analysis of the leachate from the two "blank" cells indicated that the concentration of heavy metals was about the same for the leachate collected from lined cells and the liquid portion of the raw sludge.

A comparison of the chemical analysis of the leachate from five selected liner materials and the leachate from the "blank" cells with the raw sludge solids is shown in Figure 8 for one sludge type and in Figure 9 for the other sludge type. The particular liners were selected because of the low permeability exhibited during the exposure period. It should be noted that some of the chemical parameters, i.e., magnesium, manganese, and nitrate/nitrite, have higher concentrations than that of the raw sludge. This probably can be attributed to additional accumulation of the particular elements from either the soil or liner materials.

SUMMARY

Although the data presented herein are limited to only a small portion of data collected, it is considered to be of significance if only indicating the attenuation of the concentration of heavy metals found in the leachate liquid. This could be construed that a rather high concentration is being retained in the sludge solids or in the liner materials and underlying soil. The continuation of the study through the 24-month exposure period may provide some insight for determining such a reaction. A chemical analysis of the solid portion of the sludge material retained in the test cells and of the underlying soils and liner materials may possibly clarify the matter.



CHEMICAL ANALYSIS, SLUDGE A

Sludge solids and leachate from unlined and select lined test cells, mg/l

FIGURE 8. COMPARISON OF HEAVY METAL CONCENTRATION IN RAW SLUDGE A AND LEACHATE

CHEMICAL ANALYSIS, SLUDGE B

Sludge solids and leachate from unlined and select lined test cells, mg/l

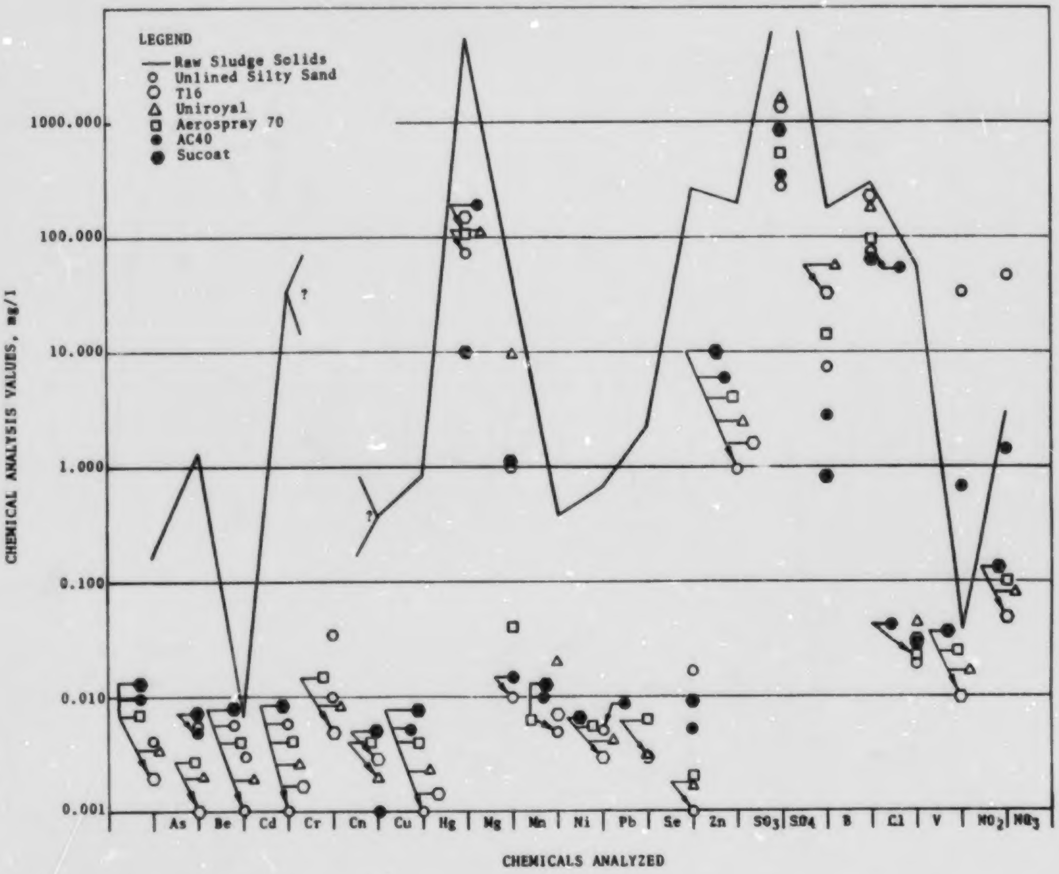


FIGURE 9. COMPARISON OF HEAVY METAL CONCENTRATION IN RAW SLUDGE B AND LEACHATE

An interim report describing the study in detail is being published. The report will present all the physical data and chemical analyses plus a few of the failures incurred.

Note: The citation of trade names listed in this paper does not constitute an official endorsement or approval of the use of such commercial products.

USE OF LIMESTONE TO LIMIT CONTAMINANT MOVEMENT FROM LANDFILLS

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ABSTRACT

Crushed limestone is an effective low-cost landfill liner aid in the migration control of certain heavy metals from solid-waste leachates. Agricultural limestone is particularly attractive as a liner because of its (a) wide geographic distribution, (b) particle sizes, and (c) relatively low cost. Limestone barriers affect the mobility of hazardous constituents by (a) adsorbing metal ions directly, (b) forming less soluble calcium and carbonate compounds, and/or (c) raising the pH level of the leachate as it passes through the limestone. Chromium changes solubility through electron change (i.e. Cr^{-6} to Cr^{-3}) at different pH values when suitable electron donors are available. Although the limestone barrier slowed the migration rate of all 12 metals studied, limestone was more effective in retention of some metals than others. Practical use of crushed limestone as liner material for landfills as an aid in reducing the migration rate of potentially toxic metal pollutants from leachates is suggested.

INTRODUCTION

The successes of Gehm (1944), Charmbury and Maneval (1967), Jones and Ruggeri (1969), Stoddard (1973), and Pearson and McDonnell (1975) and others, in the use of crushed or powdered limestone for pollution abatement management of acid mine waste provides encouragement for the use of similar materials for control of polluting constituents of other liquid wastes, such as landfill leachates. Almost all of the limestone research effort for pollution control before the early 1960's was limited to acid mine-waste management programs. During the 1970's, involvement of limestone in pollution control has rapidly expanded to fields of flue gas scrubbing. Most of this relates to desulfurization (Nannen, West, and Kreith, 1974). Lime and lime slurries are effective in the neutralization, adsorption, and precipitation of sulfur oxides and certain heavy metals. Land and lagoon disposal of the spent slurries still is required.

Limestone encasement of industrial sludges containing high concentrations of toxic metals such as has been suggested by Loughry (1972) seems to be a good program for certain sludge-like wastes. An encasement could be designed in soil trenches to retain hazardous polluting metals for a long period of time.

Using lime to minimize problems with solid waste landfill leachate, however, involves another requirement. The liquid phase should be stripped of as much of its contaminating constituents as possible before it is allowed to gravitate to lower depths where it might threaten underground water sources or enter the food chain.

One method of using lime in landfill construction would be to incorporate it into the soil at the base of the excavation. The literature on lime-soil reactions is extensive and varied in topics, as reviewed by Herrin and Mitchell (1960), Penrose and Holubec (1973) and Thompson (1964). These and other studies compiled by Jarrett (1977), however, advise against mixing lime with soils as the most desirable use of limestone for soil modification in the disposal of solid wastes on land where a "leaky-tub" effect is required. Lime mixed with soil is an effective stabilizing agent. Cation exchange, flocculation, and agglomeration may take place but they are not the basic lime-soil stabilizing reactions. Cementation that takes place when lime and carbon dioxide interact and pozzolanic reactions (Thompson, 1964) between soil silica and/or alumina and lime are generally regarded as the major sources of stabilization of the lime-soil aggregate. Since solid waste landfills that are to use the contaminant retention capacity of the soil will require a leaky bottom to avoid overflowing like a bathtub, highly compacted or cemented soils would be unsatisfactory encasement or liner structures. Moreover, dissolving of the cemented mosaics by acid activity of leachate would result in opening up the surrounding site material to stabilized cracks and fissures through which leachates could flow freely out of the landfill without first reacting with either the soil or lime liner. Another disadvantage of an intimate association between soil and limestone in humid climates is that the acid of the soil would react to consume it directly through solubilization and neutralization. Limestone has a relatively short life when used to counteract the acidity of agricultural soils. Necessary reapplications are relatively frequent, compared to the lifetime of a landfill.

Quantitative data evaluating the influence of limestone as a soil liner for landfills on the migration rates of potentially toxic pollutants of municipal solid waste are not available, except to a limited extent in a preliminary report by Fuller et al. (1977). Research was undertaken, therefore, to quantify more extensively the effectiveness of a crushed agricultural limestone layered over soil for controlling the migration rate of solutions containing selected trace and heavy metals (Be, Cr, Cd, Fe, Ni, and Zn) and total organic carbon (TOC) from municipal solid waste landfill leachate.

MATERIALS

SOILS

Eleven soils representing 7 of the major orders in the U.S. were collected below the organic-laden top soil. Although the soils were not collected entirely at depths as great as many landfills, the selection provides an opportunity for studying the effectiveness (in retarding contaminant movement) of limestone layered over soils of varying physical and chemical characteristics. If others are working with a different soil or soil-like material, they may determine the characteristics of the material and then select the most similar to the soils in this study as a base for estimating how their material will retain contaminants when limestone is used with it.

Some general characteristics of the soil collected are shown in Table 1. The clay contents range from 4 to 61%. The clay minerals of the less than 2 micron separate of the 11 soils varied widely from largely montmorillonite-type in Anthony s.l. and Chalmers si.c.l. to largely kaolinite-type in Davidson and Molokai clays and Wagram l. s. The pH values range from 4.2 for the Ultisol, Wagram l.s. to 7.8 for the alkaline Aridisols, Anthony s.l. and Mohave (Ca) c.l. Some other characteristics of the soils as packed in the columns are described in Table 2 and in an earlier published report by Fuller (1977).

MUNICIPAL LANDFILL LEACHATE II*

The leachate used as a vehicle for carrying the trace elements Be, Cd, Cr, Fe, Ni, and Zn and total organic carbon (TOC) came from a simulated municipal solid waste landfill. Leachate characteristics are reported in Table 3. The trace elements were "spiked" at concentrations of 100 ppm for all elements except iron. The Fe research was done on unspiked leachate containing variable levels of Fe up to 750 ppm as given in Table 3. Such concentrations were used for the convenience in identifying the attenuation effect of the limestone; the individual elements differ in their rate of migration through the limestone and at lower concentrations the rates of migration were too slow to allow completion of the study in a reasonable length of time.

LINER MATERIAL

The crushed limestone is a commercial product from Cedar Bluff, Kentucky, commonly used for agricultural soil applications. Particle size analysis of this 98% pure

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*Two other leachates, I and III, were used in another study (Fuller, 1978); the report of that study may be available before this paper is published.

TABLE 1. GENERAL CHARACTERISTICS OF THE SOILS

Soil Series	Soil Order	Soil Paste pH	Cation Exch Capac., meq/100g	Elec. Cond.of Extract, µmhos/cm	Column Bulk Density, g/cc	sand	Silt	clay	Texture Class	Predominant Clay Minerals*
							%			
Davidson	Ultisol	6.2	9	169	1.89	19	20	61	clay	Kaolinite
Molokai	Oxisol	6.2	14	1262	1.44	23	25	52	clay	Kaolinite, gibbsite
Nicholson	Alfisol	6.7	37	176	1.53	3	47	49	silty clay	Vermiculite
Fanno	Alfisol	7.0	33	392	1.48	35	19	46	clay	Montmorillonite, mica
Mohave (Ca)	Aridisol	7.8	12	510	1.54	32	28	40	clay loam	Mica, montmorillonite
Ava	Alfisol	4.5	19	157	1.45	10	60	31	silty clay loam	Vermiculite, kaolinite
Chalmers	Mollisol	6.6	26	288	1.60	7	58	35	silty clay loam	Montmorillonite, vermiculite
Anthony	Entisol	7.8	6	328	2.07	71	14	15	sandy loam	Montmorillonite, mica
Mohave	Aridisol	7.3	10	615	1.78	52	37	11	sandy loam	Mica, kaolinite
Kalkaska	Spodosol	4.7	10	237	1.53	91	4	5	sand	Chlorite, kaolinite
Wagram	Ultisol	4.2	2	225	1.89	88	8	4	loamy sand	Kaolinite, chlorite

*Listed in order of dominance

TABLE 2. SELECTED CHARACTERISTICS OF THE SOIL IN THE COLUMN STUDY WITH MUNICIPAL LANDFILL LEACHATE II.

Soil	Clay Content, %	Bulk Density of Column	Pore Volume, ml	Soil, grams	Total m² Surface Area	Porosity
Davidson c.	61	1.38	123	355	18,212	.476
Molokai c.	52	1.35	111	348	23,420	.429
Nicholson si.c.	49	1.38	119	357	43,019	.460
Fanno c.	46	1.42	125	367	44,811	.484
Mohave (Ca) c.l.	40	1.53	115	394	50,235	.446
Chalmers si.c.l.	35	1.42	120	366	45,970	.467
Ava si.c.l.	31	1.41	123	363	22,325	.478
Anthony s.l.	15	1.73	93	446	8,831	.360
Mohave s.l.	11	1.67	94	431	16,507	.365
Kalkaska s.	5	1.54	104	398	3,542	.404
Wagram l.s.	4	1.75	97	452	3,616	.378

TABLE 3. SOME CONSTITUENTS OF THE NATURAL MUNICIPAL SOLID-WASTE LANDFILL LEACHATE II USED IN LIMESTONE RESEARCH.

pH	EC	TC	TOC	Ca	Mg	Na	K	Cd	Co	Fe	Mn	Ni	Zn
	mmhos/cm	ppm											
5.4	8.8	7225	7007	621	116	320	641	.05	.46	753	9.8	.40	7.6

$CaCO_3$ appears in Table 4 along with two other limestones for comparative purposes. Also see Penrose and Holubec (1973) for other characteristics of limestones.

BATCH STUDIES

A series of "batch" studies was conducted prior to the more definitive column studies. The batch technique is simpler and less expensive so it was used initially to determine maximum adsorption precipitation interaction between selected trace elements and limestone. A known weight of limestone was shaken with a known volume of landfill leachate for predetermined time intervals under anaerobic conditions and CO_2 tension followed by centrifugation and analysis of the supernatant using the conventional atomic absorption flame emission. Total organic carbon was determined by a Beckman 915A Model Total Organic Carbon Analyzer.

SOIL COLUMNS

The details of the soil-column procedure have been described by Korte et al. (1976), and by Fuller (1977). In brief, soil was compacted to a uniform density in 10-cm lengths of 5-cm PVC pipe (Table 2). The top 2 cm of the column consisted of the liner limestone to be evaluated. Some columns were prepared with 5-cm of crushed limestone but movement of the trace element was so slow that this thickness was abandoned in favor of the 2-cm thickness. To evaluate the effect of the liner material independently of the soil, columns were also prepared in which acid-washed quartz sand replaced the soil.

TABLE 4. PARTICLE SIZE DISTRIBUTION OF AGRICULTURAL LIMESTONE FROM THREE REPRESENTATIVE KENTUCKY SOURCES

Sieve Size Classes			Limestone Source % of Size Separation		
φ	mm	USDA	Lexington	Cedar Bluff*	Gibsonburg
-2.5 to -2.0	- 5.66	gravel	0.89	0	0
-2.0 to -1.5	5.66-2.80		17.3	5.1	0
-1.5 to -1	2.80-2.00		13.2	4.4	0
-1 to -0.5	2.00-1.40	very coarse	15.2	6.8	0
-0.5 to 0	1.40-1.00	sand	11.4	7.8	0
0 to 0.5	1.00-0.71	coarse	10.2	8.3	0
0.5 to 1	0.71-0.50	sand	7.5	9.4	0
1 to 1.5	0.50-0.355	medium	8.3	12.5	0.3
1.5 to 2.0	0.355-0.250	sand	6.0	10.2	0.4
2.0 to 2.5	0.250-0.180	fine	3.0	6.7	1.4
2.5 to 3.0	0.180-0.125	sand	2.4	6.3	6.8
3.0 to 3.5	0.125-0.090	very fine	1.5	4.8	13.3
3.5 to 4.0	0.090-0.063	sand	1.0	6.0	13.5
	0.06-0.050		0.79	1.9	24.7
	< 0.050	silt + clay	1.22	9.9	39.5

*Limestone source used in studies reported here.

The solution carrying the spiked trace element being studied was in all cases municipal solid waste landfill leachate maintained under anaerobic conditions using CO_2. The solution was passed through the column until the effluent concentration of the spiked trace element was equal to the concentration in the influent (breakthrough).

RESULTS

NATURAL LEACHATE CONSTITUENTS

Iron

Lining soils with crushed agricultural limestone significantly delays the migration of soluble Fe of municipal solid waste landfill leachate, Figures 1 and 2. The difference between attenuation in limestone-lined and unlined soil can be even much more dramatic than these figures show, since the effluent concentration (C) of Fe in limestone-lined soils seldom reached that of the influent (C_0) before the experiments had to be terminated. $C/C_0 = 1.0$ was seldom achieved where limestone was present. The pronounced prolongation of Fe attenuation of the effluent/influent concentration ratio between ∿ 0.8 to 1.0 is illustrated at the bottom of Figure 2, where C/C_0 is plotted against number of pore volumes (pv) of solution in limestone columns alone.

The cumulative total retention of Fe attributable to the limestone liner in soil

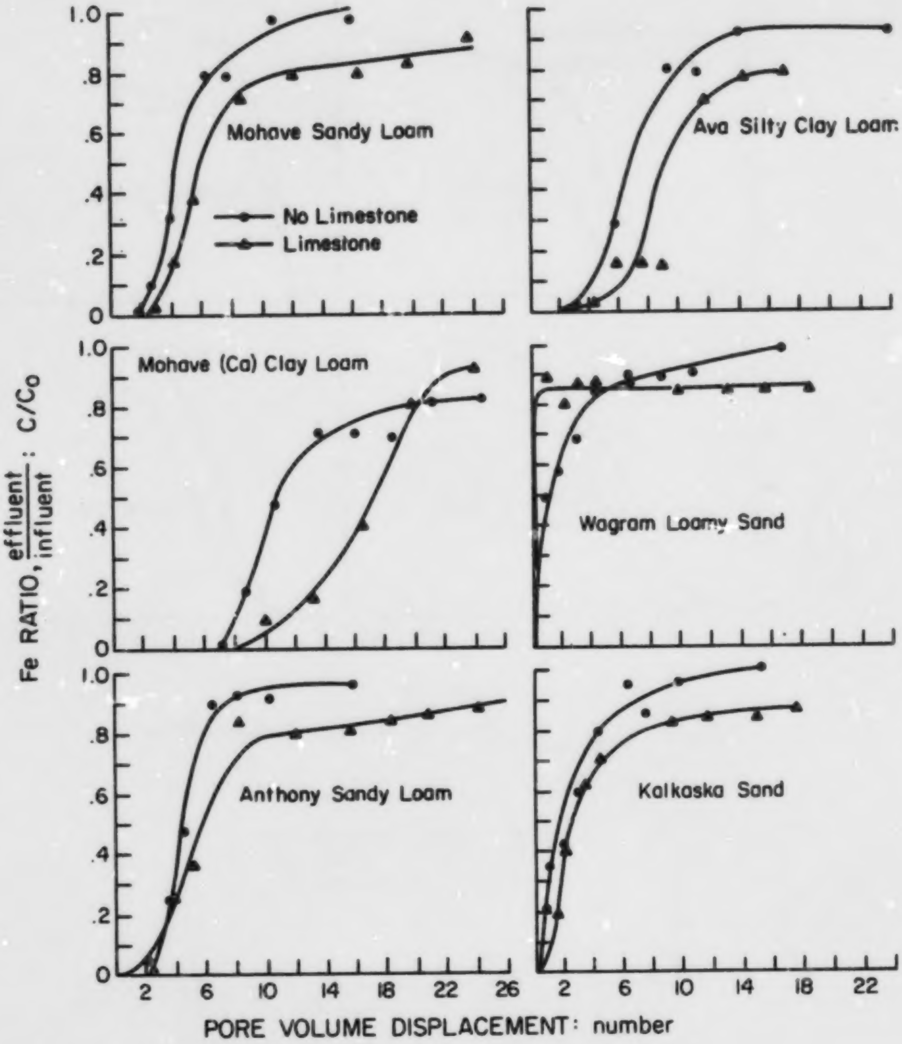

Figure 1. The effect of ground agricultural limestone layered over 6 soils on the retention of Fe from natural municipal solid-waste landfill leachate.

also is much greater than that of unlined soil, Table 5. Statistically, the F value of 96.3 is significant at the 0.01 level. There also is a significant difference between the effectiveness of different soils for retaining leachate Fe. Those soils containing the most clay held onto the Fe more tightly than the sandier soils. For example, over 90% of the leachate Fe was retained by Davidson and Molokai clays by the time C/C_0 reached 0.8, whereas the Kalkaska and Wagram sands retained less than 36% of the Fe at the same C/C_0.

After the concentration of Fe in the effluents from both lined and unlined soils stabilized at some level ranging between C/C_0 of 0.8 to 1.0, deionized water was displaced through the columns for an equal number of pvd's as the landfill leachate to ascertain the retention stability of the limestone- and soil-attenuated Fe. The re-

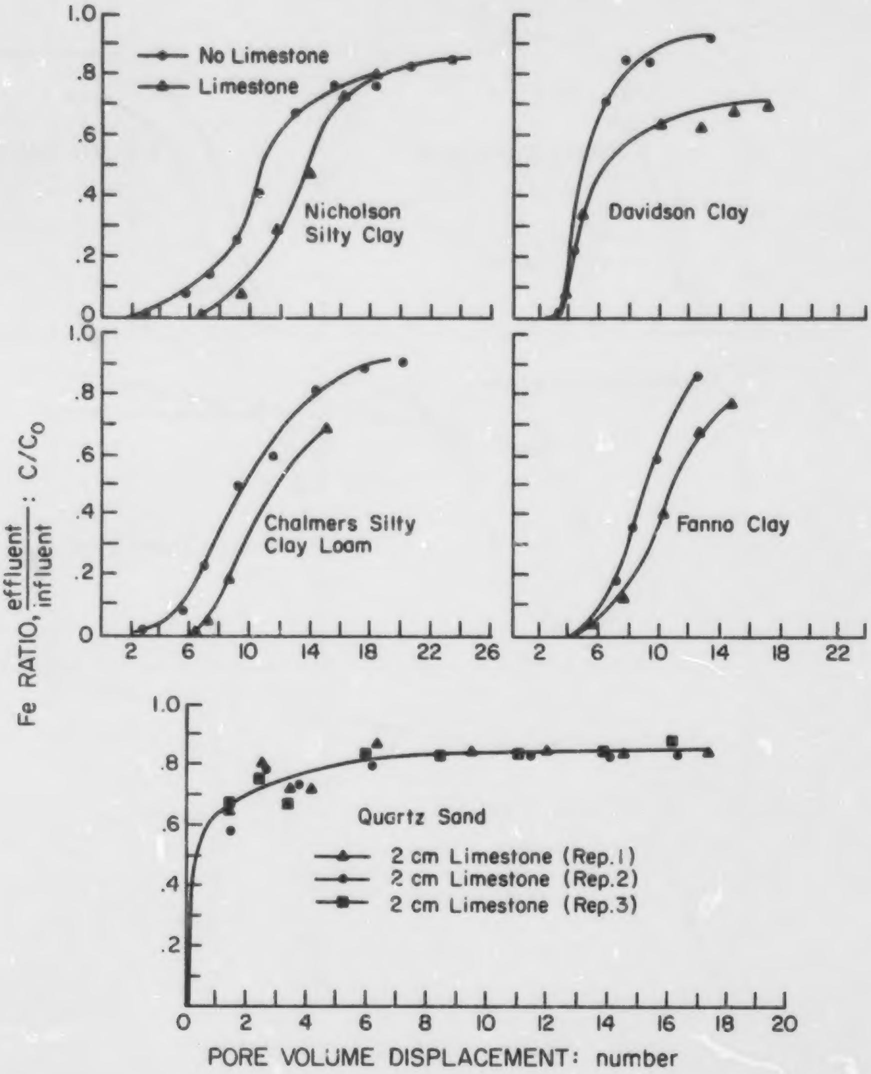

Figure 2. The effect of ground agricultural limestone layered over 4 soils and pure quartz sand on the migration rate of Fe from natural municipal solid waste landfill leachate.

sults as reported in Table 5 show that solid waste leachate Fe is rather tightly held against leaching action of water both by the limestone and soil. Only a small percentage of Fe (~ 2-7%) appeared in the effluents of the many water displacements. Even after leaching the lined and unlined columns of soil with deionized water there was still a highly significant difference in retention of Fe favoring the limestone treatment. The F value of 87.8 is well within the 0.01 level of significance.

The total retention of Fe correlates significantly with the clay content of the soils, Table 6. Davidson clay held more than 5 times as much leachate Fe per gram of soil as the sands, Kalkaska and Wagram. The 9-fold difference between Molokai clay and the same sands is even more dramatic. Based

TABLE 5. EFFECT OF CRUSHED LIMESTONE LINER ON THE RETENTION OF SOLUBLE IRON FROM NATURAL MUNICIPAL SOLID WASTE LANDFILL LEACHATE PASSED THROUGH 11 SOILS.

		Soluble Landfill Leachate Fe Retained in Soil Column - %			
		With Limestone Layer-2cm		Without Limestone Layer	
Soil	Pore* Volume	Before H_2O Leach	After† H_2O Leach	Before H_2O Leach	After† H_2O Leach
Davidson c.	25	94	91	64	59
Molokai c.	20	97	96	71	65
Nicholson si.c.	18	82	79	68	65
Fanno c.	12	82	80	62	61
Mohave (Ca)	20	83	82	62	61
Chalmers	18	74	71	52	51
Ava si.c.l.	16	70	68	44	40
Anthony s.l.	11	51	48	41	36
Mohave s.l.	16	44	41	34	31
Kalkaska s.	15	36	33	20	13
Wagram l.s.	17	34	31	15	12

*Pore volume refers to breakthrough where $C/C_0 \approx 1.0$ or at peak C/C_0 plateau between 0.8 and 1.0.

†Soil columns were leached with deionized water by equal number of pvd as used for landfill leachate.

TABLE 6. ATTENUATION OF IRON IN NATURAL MUNICIPAL LANDFILL LEACHATE II PASSED THROUGH 11 SOILS AS RELATED TO UNIT WEIGHT AND SURFACE AREA.

			Fe Attenuated†		
Soil	Clay Content %	Pore Volume Displacements*	Total Fe, mg	Fe mg/g Soil	Fe µg/m² Surface Area
Davidson c.	61	25	922	2.597	51
Molokai c.	52	20	1671	4.803	71
Nicholson si.c.	49	18	1024	2.868	24
Fanno c.	46	12	899	2.450	20
Mohave (Ca) c.l.	40	20	1061	2.962	21
Chalmers si.c.l.	35	18	889	2.448	20
Ava si.c.l.	31	16	680	1.874	30
Anthony s.l.	15	11	383	1.491	28
Mohave s.l.	11	16	470	1.090	28
Kalkaska s.	5	15	289	0.545	61
Wagram l.s.	4	17	251	0.555	69

*Pore volume displacements necessary to achieve breakthrough (i.e. $C/C_0 = 1$) or at peak C/C_0 plateau between 0.8 and 1.0.

†mg Fe attenuated = mg Fe added - mg Fe in leachate effluent.

on surface area, clay again appears to be a very effective attenuator compared with sand or silt. The relatively high values of Fe held per unit of surface area for Kalkaska and Wagram sands make it seem that these sands have unusual surface activities. The data in these cases are misleading, since landfill leachate collected under CO_2 and displaced through soil in this condition always will form some precipitation even along the tubing approaching the soil column from the reservoir. The precipitation becomes more prominent at each successive leachate displacement through the columns. Furthermore, columns of glass beads of relatively small surface area have been observed to collect a certain amount of Fe precipitation. If it were possible to arrive at a quantitative figure for this kind of precipitation (unrelated to surface area), no doubt sands would be shown to possess less active surfaces than clays per unit area. This is a small point in view of the great difference between total surface area per unit weight of sand and clay.

Total Organic Carbon

The soluble organic carbon constituents of natural municipal solid-waste landfill leachate II were not retained to any significant extent by soil or crushed limestone, Table 7. Limestone liners do not have enough effect to be considered as a management practice for TOC control in landfill sites.

METALLIC CATIONS

Be, Cd, Ni and Zn

Because the landfill leachate must pass through the limestone barrier prior to contacting the soil, a batch-type experiment was developed. The influence of time of contact, ratio of leachate to water (simulated rain water dilution effect), and pH were studied between the limestone and leachate alone. The resulting data should represent maximum reactions between the two systems. Figure 3 reveals the limestone/leachate reactions with Cd were significantly dependent on (a) contact time, (b) leachate concentration, and (c) leachate pH level. Sorting out the precise cause and effect relationship between these three factors and attenuation would be difficult because of their interdependence. From a standpoint of actual landfill leachate management alone, this batch-type research is more academic than practical. However, it serves to point out possible profitable departures for the more practical research program.

The effect of crushed limestone placed as a liner barrier over soils on the retention of Be, Cd, Cr, Ni, and Zn contained in municipal solid waste landfill leachate varies both with the kind of soil and metal, Table 8. (Breakthrough was not achieved in every column.) For example, to achieve the same C/C_0 of Be, Davidson clay (soil 1) required 30 pv in the presence of limestone and only 10 in its absence. Cadmium, on the other hand, was less well retained by limestone when associated with Davidson clay than Be since the difference between limed and unlimed soil was only 14 pv. The data make it quite clear that limestone can have a highly significant effect on the migration rate of the metals tested even though only a thin liner of 2 cm was used. Had there been sufficient time to conduct column studies with limestone layers thicker than a few centimeters, the barrier effect of limestone might have been more dramatic. For example, the 5 cm of limestone used in preliminary experiments was so effective in retaining the metals, months went by with little evidence of the test element appearing in the effluent. The program for that thickness had to be abandoned (with the concentrate leachate II available) because no data were being generated for comparative purposes. The data in Table 8, therefore, are relative and will serve a practical purpose for liner management if used with this understanding (i.e., the effectiveness is directly related to and proportional to the thickness of the crushed limestone. Conceivably, such a thickness may be used to keep any toxic element from migrating for infinite time. Practical application, however, may not prove out so well if ideal conditions can't be maintained.)

ANION-FORMING METAL

Chromium

The influence of limestone liner on Cr retention is much greater than that for the other metals tested, Table 8. This occurs, however, at lower pH values of the influent leachate necessary to keep Cr in solution at a constant concentration. Migration rate of Cr through both the limestone-lined and unlined soil columns was significantly greater

TABLE 7. EFFECT OF GROUND LIMESTONE LINER ON THE RETENTION OF SOLUBLE ORGANIC CARBON (TOC) CONSTITUENTS FROM NATURAL MUNICIPAL SOLID WASTE LANDFILL LEACHATE PASSING THORUGH SOIL AND SAND

Pore Volume Displacement Number	TOC - ppm*					
	Soils					
	Davidson	Molokai	Nicholson	Fanno	Mohave(Ca)	Chalmers
1	4000	6400	6400	6800	7400	6500
2	5300	6300	5900	6800	6300	6600
3	6400	6700	6300	6600	6600	5700
4	6500	6600	6400	6500	6600	6000
5	6850	6500	6300	6600	7200	6200
6	6700	6600	6300	6700	6900	5800
7	6800	6200	6400	6600	6200	5600
8	6800	6200	6500	6500	6400	6100
10	6900	6100	6900	7300	6500	--
12	7000	6800	7300	7200	7200	--
14	7000	7000	6900	7100	7300	--
16	7000	7100	6600	--	6700	--
18	--	7100	--	--	6700	--
20	--	7100	--	--	6700	--
	Ava	Anthony	Mohave	Kalkaska	Wagram	Quartz sand
1	4600	7300	7600	6800	5550	6800
2	5100	6800	6400	6400	6000	6200
3	6000	6300	6500	6900	6900	6400
4	6800	6700	6600	7000	6300	6800
5	6750	7000	6800	7000	6600	6900
6	6700	7100	6800	6900	6700	7000
7	6700	6700	6700	6800	6800	7000
8	6800	6800	6400	6900	6800	7100
10	7000	6600	6500	7300	6800	6900
12	7200	6400	6600	7300	7300	6900
14	6900	7000	7000	7300	7600	6900
16	6900	7300	7400	7300	7300	6900
18	--	7300	7400	7300	6800	7000
20	--	7300	7400	--	--	7000

*Natural influent leachate contained ∿ 7000 ppm TOC

at pH 2.5 than a 4.0. The difference is thought to be due to an e^- effect on the proportion of CrIII to CrVI. Higher pH levels favor a shift in concentration of chromium from the more soluble Cr to the less soluble Cr (Artiola and Fuller, 1978). Limestone also contributes to this shift because of its effect on pH.

There appears to be a combined influ-

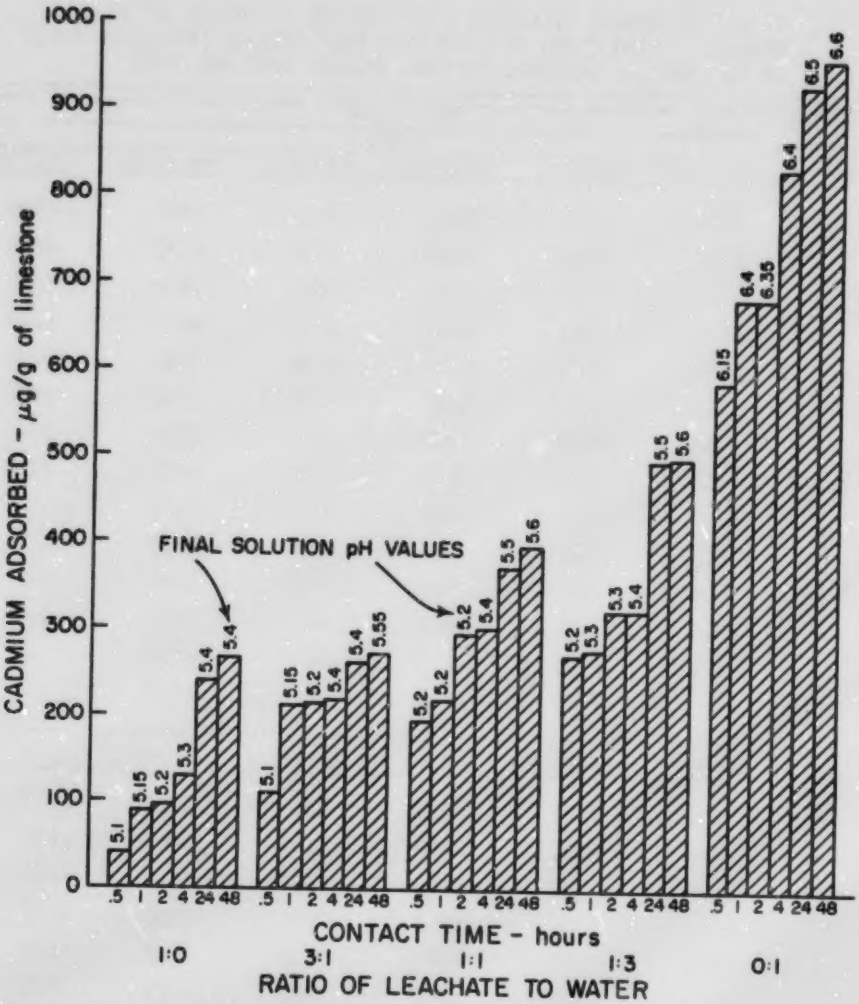

Figure 3. The influence of time of contact, ratio of municipal landfill leachate to water, and pH in the adsorption of Cd by agricultural limestone (Cd concentration in all solutions at 100 ppm after water dilution).

ence on retention of Cr between the limestone liner and soil not apparent when leachate was passed through limestone and soil independently, Table 9. At Cr C/C_0 = 1.0, the difference between soil alone and limestone alone for Anthony s.l., Kalkaska s. and Wagram l.s. was 29, 37, and 37 pvd, respectively. The difference for Mohave s. l. is even greater. Explanation for the reactions or mechanism involved is not available at this time since this effect occurred with all limestone-lined soils and irrespective of spiked metal or constituents of unspiked natural municipal leachates.

LIMESTONE UTILIZATION

The length of time limestone liners will remain active in landfills determines their practicality for immobilizing or stabilizing potentially hazardous pollutants. A balance sheet was, therefore, maintained to accurately account for the Ca in the influent and effluent of the soils, while leachate displacement was going on. Since the crushed agricultural limestone contained 98% $CaCO_3$, the Ca calculated as difference between column input and output minus soil-Ca was converted back to lime-

TABLE 8. RELATIVE EFFECT OF CRUSHED LIMESTONE LINER PLACED OVER SOIL ON THE PREVENTION OF HEAVY METALS, IN MUNICIPAL SOLID WASTE LANDFILL LEACHATE, FROM MIGRATING.

	Pore Volume Displacement to Achieve the Same C/C_0											
	With Limestone Layer with Soil						No limestone Layer, Soil Only					
Element	1*	2	3	4	5	6	1	2	3	4	5	6
Be	30	29	35	30	30	25	10	16	15	15	18	10
Cd	30	35	40	38	35	35	16	18	28	15	18	6
Cr(pH 2.5)	35	42	85	88	86	65	10	15	5	10	10	6
Cr(pH 4.0)	28	49	125	144	111	109	2	21	39	25	17	15
Fe	31	31	35	36	30	25	21	26	10	25	10	10
Ni	40	35	30	35	28	24	20	15	11	15	7	10
Zn	30	25	30	32	25	30	10	11	15	18	12	16

*Numbers refer to: 1 = Davidson c.; 2 = Ava si.c.l.; 3 = Anthony s.l.; 4 = Mohave s.l.;
5 = Kalkaska s.; 6 = Wagram l.s.

TABLE 9. EVALUATION OF THE EFFECTIVENESS OF AGRICULTURAL LIMESTONE ALONE AND LIMESTONE LAYERED OVER SOILS FOR ATTENUATION OF CHROMIUM IN MUNICIPAL SOLID-WASTE LANDFILL LEACHATE II*

	Soil		Ratio of Cr in Influent & Effluent, C/C_0	Pore volume displacement number when Cr concentration in effluent is at C/C_0 given in Column Four		
Series	Clay, %	pH		Limestone Alone	Soil Alone	Soil and Limestone
Davidson c.	61	6.2	0.13	2	2	28
Ava si.c.l.	31	4.5	0.38	5	21	49
Anthony s.l.	15	7.8	1.00	57	39	125
Mohave s.l.	11	7.3	0.76	46	25	144
Kalkaska s.	5	4.7	1.00	57	17	111
Wagram l.s.	4	4.2	1.00	57	15	109

*Leachate II had a pH value of 4.0, TOC of > 3000 and Fe = 300 ppm.

stone $CaCO_3$. The limestone liners were consumed as a result of leachate interactions, Table 10. The rate of loss depends primarily on time and pH or acidity of the landfill leachate. For example, approximately twice as much limestone was solubilized at 90 pvd when the leachate pH was 2.5 as at 4.0. It took about 150 pvd of pH 4.0 leachate to cause the same loss of limestone as 90 pvd with the pH 2.5 leachate. With natural (unadjusted) leachate at pH 5.4 utilization of limestone was still less. Averages for the 6 soils at 20 pvd was 19.1, 8.4, and 1.8 percent for the pH 2.5, 4.0, and 5.4 leachates, respectively. The utilization of limestone alone in a 2-cm layer placed between pure quartz sand layers by the pH 4.5 leachate is shown in Table 11 to be in between that solubilized at pH 4.0 and 5.4 reported in Table 10. The Ca in the effluent decreased with time and the Fe increased slightly under these conditions.

TABLE 10. EFFECT OF MUNICIPAL LANDFILL LEACHATE pH ON THE LOSS OF LIMESTONE USED AS LINERS OVER SOIL.

Pore Volume Displacement Number	Soils					
	Davidson	Mohave	Ava	Anthony	Kalkaska	Wagram
	Limestone Loss - %					
	Leachate pH adjusted to 2.5*					
1	0.4	0.6	0.1	0.9	0.5	0.5
10	7.9	4.1	14.8	6.3	5.4	8.8
20	15.0	24.3	24.0	14.8	16.5	20.1
30	21.1	19.8	31.5	21.4	22.8	26.0
40	--	25.0	--	25.6	28.9	30.9
50	--	29.5	--	32.1	34.4	34.4
60	--	33.5	--	36.0	38.8	31.3
70	--	36.8	--	39.1	41.5	41.0
80	--	39.1	--	40.9	43.5	43.1
90	--	39.9	--	41.1	45.1	44.2
	Leachate pH adjusted to 4.0*					
1	0.1	0	0.3	0.4	0.3	0.4
10	5.9	4.8	6.0	2.9	3.9	4.8
20	9.0	7.9	10.0	7.6	7.6	8.1
30	10.5	11.3	13.1	10.6	11.3	11.3
40	11.4	13.9	15.8	13.9	15.1	14.0
50	--	16.5	--	17.0	18.3	16.9
60	--	18.8	--	20.0	21.9	19.6
70	--	20.9	--	23.1	25.0	22.3
80	--	23.1	--	26.0	28.4	25.0
90	--	25.1	--	29.0	31.5	27.6
100	--	27.1	--	32.0	34.3	30.1
110	--	29.1	--	34.8	36.6	32.5
120	--	30.9	--	37.5	38.6	35.2
130	--	32.8	--	39.9	39.9	37.4
140	--	34.4	--	42.1	2.5	40.2
	Leachate pH 5.4 (not adjusted)†					
1	0.3	0.5	0	0.3	0	0.1
2	0.6	1.0	0	0.5	0	0.3
3	0.8	1.2	0	0.8	0.1	0.4
4	0.9	1.3	0	0.9	0.2	0.5
6	1.1	0.6	0.4	1.2	0.3	0.6
8	1.3	1.8	0.7	1.5	0.5	0.8
10	1.5	2.0	0.9	1.7	0.6	1.0
12	1.6	2.2	1.0	1.8	0.8	1.0
14	1.7	2.3	1.2	1.9	0.9	1.1
16	1.8	2.4	1.3	2.0	1.0	1.2
18	1.9	2.5	1.4	2.1	1.0	1.3
20	2.0	2.6	1.5	2.2	1.1	1.4

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[*] pH was adjusted with HCl to aid in evaluating leachate pH effects on limestone utilization or loss.

[†] Original leachate, pH = 5.4.

pH levels of 2.5 and 4.0 fall below those of most municipal solid-waste landfill leachates reported in the literature (Garland and Mosher, 1974; and Chain and DeWalle, 1976). However, the pH of some industrial leachates may fall well below these values.

TABLE 11. IRON AND CALCIUM CONTENT OF EFFLUENT FROM LIMESTONE LINER-QUARTZ SAND COLUMNS INFILTRATED WITH MUNICIPAL LANDFILL LEACHATE at pH 4.5 and the CONCURRENT LIMESTONE LOSS.

Pore Volume Displacement	Fe, ppm	Ca, ppm	Limestone Lost g	Limestone Lost %
1	1.5	1250	0.2	0.25
9	5.0	1224	2.3	2.88
19	6.5	1225	4.7	5.88
28	4.0	1170	7.0	8.75
38	8.0	1100	9.5	11.88
48	7.0	1100	12.2	15.25
60	9.0	995	13.8	17.25

Average of 3 closely agreeing limestone columns.

CONSIDERATION IN USE OF LIMESTONE LINERS

Research with soil columns and crushed limestone has identified factors that must be considered if a disposal operation is to be successful in avoiding water contamination. At some ideal disposal sites, the soil alone may restrict contaminant movement sufficiently to prevent water contamination. However, it is difficult to identify, with certainty, an ideal site and even at ideal sites the use of limestone liners will be required. For limestone use to be successful, the following factors should be considered:

1. Kind and depth of soil selected for disposal site.

2. Characteristics of the leachate generated or to be deposited.

3. Characteristics of the specific potentially hazardous pollutants.

4. Peculiarities of limestone and its reactions with leachate constituents.

5. The environment (climate, depth to water table, etc.)

SOIL

Regardless of the characteristics of the disposal site, inclusion of limestone alone can slow the migration rate of heavy metals through soil. Our experiments indicate, however, that limestone varies considerably in degree of effectiveness for controlling migration of potentially hazardous metals in leachates depending on the way it is associated with soil as well as the kind of soil involved. Soil texture is one of these factors. Limestone appears to be more effective with clayey than sandy soils, provided of course the clay is permeable to water. Soils unusually high in clay, however, may clog with degradation constituents created in reactions with limestone. This brings into focus the factor of structure or pore space distribution in soil. Despite the favorable reaction of the divalent Ca ion (solubilized from the added limestone) on soil structure, the reprecipitation of Ca as $CaCO_3$ and/or other reaction products at lower depths in the soil remains a possibility to be considered. An open-structured soil, therefore, is favored over a tightly structure soil as site material.

Layering or lining soil is preferred to mixing limestone with soil. Intimate mixing results in soil stabilization or cementation which at first will block the movement of the solution from leaving the site and at a later date encourage the formation of fixed channels (holes) through which solutions can move into the natural soil or geologic debris without first having reacted with the barrier material. Examples of this problem are well documented. Where landfills have been located over thick layers or natural limestone deposits, the leachates follow down cracks and holes to some lower depth virtually unchanged. Moreover, mixing limestone with soil, particularly in humid regions where soils are acid, results in the loss of limestone to neutralization of the highly buffered medium. The life of the limestone, under such conditions, is greatly shortened.

One of the encouraging results of the limestone research is the discovery of a synergic effect. Attenuation of the leachate metals is greater when soil and limestone (as a liner) are together than the sum of attenuation of both when they are kept separate. Such findings lend support to the practice of lining limestone over soil rather than using other methods of application. It does not preclude, however, a possible advantage of adding some limestone directly to landfills at different stages of deposition of refuse, to neutralize the acids. Additional research needs to be undertaken to justify such a practice. Limestone was observed in the batch studies to cause some organic material as well as inorganic elements to flocculate and precipitate.

LEACHATE

The single most important characteristic of leachate that influences the rate of metal migration through limestone-lined soil is acidity (or pH). By reducing acidity (i.e. raising the pH) migration rate can be lessened severalfold. Therefore, any practice (such as aeration) that results in raising the pH toward neutrality may be expected to enhance the effectiveness of the limestone and prolong its life.

Leachates high in total organic carbon constituents and soluble salts (or IONS) possess a greater limestone requirement than more dilute leachates because of their known higher buffer capacity. From a practical standpoint limestone lining alone may be effective as a barrier to undesirable migration of metals from dilute, older leachates. Fresh or highly concentrated leachate, on the other hand, may be only temporarily controlled by limestone lining. Additional control measures may be needed for full control. Exploratory soil column studies on a laboratory scale may be necessary to determine what level of leachate concentration would break through the barrier under the specific environmental conditions of the disposal site (e.g. high rainfall and acid soil conditions).

LIMESTONE

Variations in particle size distribution of crushed limestone, within the range reported in Table 4 did not result in differences in the retention of the elements studied (Fuller et al., 1976). It was concluded that particle size was not critical as long as particles ranged between sizes of gravel and coarse sand. Thick layers of fine particles seriously clog and finally compact into an impervious layer. Therefore, coarser size grades should be utilized particularly when (a) leachates are high in soluble constituents (organic and inorganic) and (b) when thick layers in excess of 5 cm (2 inches) are required.

The quality of limestone varies from place to place. Dolomitic limestone (magnesium carbonate) is less effective than calcium carbonate limestone. Magnesium carbonate reacts more slowly and often incompletely with acids of the leachate and may form slick, bulky colloids with organic and inorganic constituents that clog and seal the disposal lining. Silicates associated with limestone also may cause infiltration problems. Since these and other constituents often found deposited with limestone may have an adverse effect on the quality of lining, only high quality $CaCO_3$ limestone should be used.

Thickness of limestone liners requires a judgment decision. Because leachate composition varies so widely and because we have been unable to quantitatively relate leachate quality, liner thickness, and contaminant retention by mathematical equation, no single threshold thickness for all landfills can be provided. Obviously the 2-cm layer used in our experiments is too thin for practical disposal operations. Necessary traffic over such a thin layer would disrupt continuity and provide escape channels through the intended barrier. A minimum limit of thickness may be near 13 cm (5 in.) and a maximum near 30 cm (12 in.) depending on particle size distribution. Field experiments must determine the most effective thickness under conditions at an actual field disposal site. Excessive depths of limestone lining may prove unsatisfactory because of compaction, cementation and reactions that seal the site from solution infiltration.

ELEMENT

Specific elements react differently with limestone. Individual differences, however, may be modified, even to the extent of complete masking, by (a) high concentration of soluble constituents in the leachates that compete for the same reactions and adsorption sites and (b) dilution effect of both the associated solid and liquid phases of the system. Such anion elements as Cr that undergo valency changes readily, respond more acutely to limestone than the cations (Be, Cd, Ni, Zn). From a management standpoint, limestone use in Cr disposal has a great chance of successful control and therefore should be given top consideration.

ENVIRONMENT

Site selection is an all-important part of land disposal management. Environmental factors such as depth and nature of soil and/or geologic debris, at the disposal site, rainfall quantity and intensity, seasonal temperature means, slope of land, runoff and erosion hazard, and depth to underground water must be assessed in relation to their impact on the effectiveness of the limestone liner use. Design of a liner must relate to the disposal site environment.

SUMMARY

These laboratory studies indicate that the use of crushed limestone linings on the bottom of municipal solid waste and other types of landfills will significantly retard the movement of some contaminants into and through underlying soils. The movement of metallic cations such as Be, Cd, Fe, Ni, and Zn and anions such as Cr in leachate is retarded; movement of the total organic carbon (TOC) fraction of municipal solid-waste leachate is not retarded by limestone linings. Characteristics of the underlying soil affect the effectiveness of a limestone liner. Increased protection from a liner is greater in finer textured soils (clays, loams, etc.) than in coarser textured soils (sands, sandy loams, etc.). The relationship between leachate characteristics, thickness of the limestone liner, soil characteristics, and the degree to which contaminant movement is retarded is complex; a quantitative measure of this relationship and of the effective life of a limestone liner could not be developed. Additionally, due to problems from compaction and plugging, there may be operational limitations (under field conditions) on the maximum thickness of a limestone liner. No field data are available to evaluate this problem.

Using the data in this paper (volume and characteristics of leachate, limestone and soil thickness, limestone and soil characteristics) estimates of limestone thickness required at a proposed landfill can be made, provided information is available on the soil and the expected leachate characteristics at the site. Although inclusion of limestone in landfill design will clearly decrease certain types of environmental impacts, such design estimates will be qualitative judgments and should not be expected to provide an exact degree of protection.

ACKNOWLEDGMENT

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PILOT SCALE EVALUATION OF DESIGN PARAMETERS FOR SORBENT TREATMENT OF INDUSTRIAL SLUDGE LEACHATES

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ABSTRACT

Based on laboratory lysimeter studies an outdoor pilot scale sized lysimeter was designed and utilized for the sorbent treatment of leachate resulting from a calcium fluoride sludge.

Results of the laboratory lysimeter experiments indicate sorbent capacity is a function of the pH and concentration of the particular contaminant in the leachate with the volume of leachate that can be treated with maximum removal being regulated by the velocity through the bed. Velocity of the leachate can be influenced by a number of factors such as bed height, particle size and addition of inert material. Effective treatment of calcium, copper, cyanide, fluoride and COD was achieved.

INTRODUCTION

The purpose of most waste treatment processes is to convert the pollutants into a gas, such as carbon dioxide, or into a solid which can be readily removed from the waste streams. In the latter instance, the end product is a sludge which must be disposed of in an environmentally acceptable manner. At the present time, ocean dumping and landfill are the two most common methods being utilized for the disposal of this sludge. However, ocean dumping is to be banned by congressional action in 1981; thus, landfill will be the remaining receptacle for these sludges.

Disposal of sludges by landfilling can lead to heavy metal, toxic anion and organic contamination of surface and ground waters by leachate which results from ground water seepage or rainwater filtration through these sludges. In general, this contamination can be minimized by 1) respective location of the landfill so that the natural clay components in the soil can attenuate the pollutants in the leachate or 2) lining the landfill site with an impermeable membrane to prevent groundwater intrusion into the site, collecting the leachate resulting from rainwater filtration through the sludge and treating it by conventional physical-chemical treatment (i.e., activated carbon and alumina). While this latter approach is expensive because of the attendent cost required for the regeneration of these refined sorbents, it provides for treatment of the leachate before it leaves the landfill site and minimizes the dependence on natural attenuation in soil which is, in general, considered unreliable.

The identification and utilization of inexpensive clay and waste product sorbents which could be used to replace the refined sorbents (i.e., activated carbon and alumina) would eliminate the need for sorbent regeneration facilities and provide a system for treatment of the leachate at the site that is economically attractive.

A number of investigators have shown that in leachates and waste streams, organics (e.g., phenols[1], surfactants[2], pyridine[3,4], other organics characterized by COD[5]), pesticides (e.g., parathion[6], DDT, dieldrin and heptachlor[7]), herbicides (e.g., paraquet[8]), heavy metals (e.g., lead, cadmium, mercury, zinc, mangenese, copper[9,10,11,12,13] and toxic anions (e.g., chromium VI, arsenic and selenium[14]) are attenuated by clay minerals, soils and waste products[15]. However, none have explored the use of fly ash-clay sorbent mixtures to define the most effective combination for the removal of heavy metals, toxic anions and organics from leachate, identified engineering parameters required for design of the treatment system using these sorbent combinations and controlled the background leaching of heavy metals encountered when fly ash, illite and kaolinite[16] are used as sorbents.

This investigation has been concerned overall with: (1) defining the clay-fly ash combinations which are most effective in removing the heavy metals, toxic anions, and organics present in leachates originating from industrial sludges; (2) examining the effect of such factors as pH of the leachate and velocity of leachate through the sorbent on removal of contaminants; and (3) establishing a design approach for this treatment. Item (1) and part of item (2) have been investigated earlier. This involved a laboratory evaluation of the natural sorbents, vermiculite, illite, kaolinite, acidic and basic fly ashes, and zeolite for the removal of cations, anions and organics under flowing conditions from an acidic petroleum sludge leachate, a neutral calcium fluoride sludge leachate, and an alkaline metal finishing sludge leachate. Activated alumina and activated carbon were involved in this study for comparison purposes since these materials are commonly used for the treatment of industrial waste streams.

The results of this investigation indicate that rather than a single sorbent, a combination of acidic and basic sorbents (which induce acidic and alkaline conditions respectively into the leachate) is required in a layered system for the removal of all the measurable contaminants present in the leachates. These are illite, vermiculite and zeolite for the acidic leachate, illite, acidic fly ash and zeolite for the neutral leachate and illite, kaolinite and zeolite for the alkaline leachate based upon a comparison of their sorbent capacity (total amount of specific cations, anions or organics removed by a gram of each sorbent). The sorbent capacities exhibited by the natural sorbents for the removal of the cations, anions and organics in the leachates are comparable to those exhibited by the refined sorbents (i.e., activated carbon and alumina). Also, pH control of the leachates by combined use of the acidic and basic sorbents is essential for effective treatment. The removal of the anions in the leachates are favored by acidic conditions, the cations by basic conditions and the organics either by acidic or basic conditions.

It was the purpose of this study to further define the process controlling parameters using laboratory lysimeters and to carry out a pilot scale study for the treatment of calcium fluoride sludge leachate using the fly ash-clay sorbent combinations. The calcium fluoride sludge leachate was selected for the pilot study since the levels of fluoride in this leachate were in the 5 to 20 ppm range and there is no inexpensive treatment process presently available to reduce the fluoride concentration to 1 mg/l or less.

The aims of the laboratory lysimeter studies which were conducted were: (1) identify the most effective sorbent combinations for the treatment of the calcium fluoride sludge leachate; (2) determine that velocity of leachate through the sorbent bed which provides the most effective removal of fluoride; and (3) to install outdoor lysimeters and evaluate the most promising sorbent combination, based on the laboratory lysimeter studies.

EXPERIMENTAL

The preparation of the industrial sludge leachates, as well as the analytical and laboratory lysimeter procedures used in this study have been discussed previously[16,17].

In order to evaluate the use of the clay-fly ash combination for the treatment of industrial sludge leachates on a pilot scale, two large vertical lysimeters were set up outdoors. This outdoor system consisted of an agitator, filtration column, storage, and constant head lysimeter. (See Figure 1).

Calcium fluoride sludge was collected from the same source over a period of a year to take advantage of changes in production schedules and processes which could lead to compositional changes in the leachate. In this manner, the effect of compositional changes on the removal of the cations, anions and organics by the natural clay-fly ash sorbent combinations could be studied.

The preparation of sludge leachate for the outdoor study was as follows: a sample of each batch of sludge was dried at 103°C to constant weight in order to determine its moisture content. The unaltered sludge was then mixed with water in a ratio of 2.5 ml water per gram of dried sludge and mechanically stirred for 24 hours. The resultant mixture was then filtered through a multimedia filtration bed. The filter bed, which was housed in a stainless steel column, consisted of four layers of filter sand and gravel. The top layer was uniform medium gravel with D_{50} = 19.1 mm and a thickness of 7.6 cm; the second layer from the top was a fine gravel with D_{85} = 16.8 mm and D_{15} = 14.2 mm, and a thickness of 7.6 cm; the third layer was a coarse sand with D_{85} = 6.3 mm and D_{15} = 5.1 mm and a thickness of 10.2 cm; the fourth layer was medium sand with D_{85} = 1.47 mm and D_{15} = 1.2 mm and a thickness of 10.2 cm and the bottom layer was #20 - #30 Ottawa sand with D_{50} = 0.715 mm and a thickness of 22.9 cm. This arrangement of gravel and sand in the filter bed was based on the results of a series of measurements made using different sizes of gravel and sand and was designed to provide an effluent whose suspended particles would not clog the bed.

The outdoor lysimeters were constructed of P.V.C. tubing (56 cm O.D. with a wall thickness of 4.8 mm and 153 cm length) supported by lucite plates in a vertical position. The general configuration and features of the field lysimeter are similar to those of the laboratory lysimeters previously described[16]. The use of identical lysimeters provided a measure of the reproduceability of the sorbent system. Both lysimeters were packed with the preweighed sorbents, sufficient to treat 140 gallons of leachate. Five to 10 cm of Ottawa sand was placed below and above the sorbents to prevent disturbing the geometry of the sorbents during addition of leachate. Leachate was fed to the top of the column through a valved manifold which distributed this to both lysimeters, simultaneously, from the storage reservoir. The lysimeters were designed for constant hydraulic head. Thus, overflow from the constant head drain was collected and pumped back to the storage reservoir. All tubing in the system was made of Tygon tubing (9.6 mm I.D.). The effluent volume was monitored as a function of time and samples of leachate effluent analyzed at intervals to determine the con-

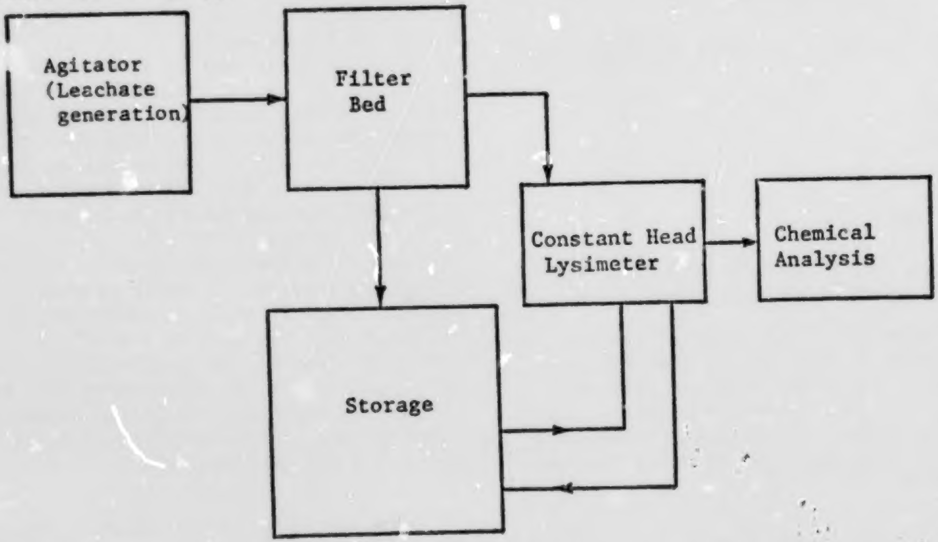

Figure 1 - Schematic Diagram of Pilot Scale Study

centration of all measurable constituents remaining in the effluent after a known volume of leachate had passed through the column. This was continued for three different calcium fluoride sludge leachates collected from the same source at different times.

A stainless steel 50 gallon tank equipped with drainage outlet was used as storage tank. This storage tank was located between the filter bed and field lysimeters to serve as both a reservoir and overflow receiver.

Results and Discussion

In order to carry out pilot scale studies on the treatment of calcium fluoride sludge leachate, it was necessary to identify the most promising sorbent combinations and determine the velocity of leachate through the sorbent bed which provides for the most effective removal of fluoride.

Laboratory Study

Analysis of the leachate used in the laboratory study is presented in Table 1.

TABLE 1

ANALYSIS OF THE NEUTRAL CALCIUM FLUORIDE SLUDGE LEACHATE USED FOR OBTAINING SORBENT COMBINATIONS TO PROVIDE OPTIMUM TREATMENT

Measured Pollutant[1]	Concentration (mg/l)
Ca	119
Mg	89
Zn	0.31
F	15.5
CN	0.61
COD (Organics)	36

[1] Cd, Cr, Cu, Fe, Ni and Pb were analyzed for, but found to be below measurable levels.

In this table are listed the pollutants whose concentrations in the leachate were at measurable levels. The leachate was also analyzed for cadmium, chromium, copper, iron, nickel and lead but these heavy metal ions were found to be below measurable levels.

This leachate was passed through laboratory lysimeters that contained varying amounts of the two most promising sorbent combinations[17], illite, acidic and basic fly ashes or illite, acidic fly ash and zeolite. The sorbent combinations were placed in lysimeters in a layered system in the weight ratios of 1:1:1 or 2:2:1, with the illite being the top layer followed by acidic fly ash or visa versa and either basic fly ash or zeolite forming the bottom layer. The basic fly ash or zeolite was placed at the bottom to remove the cations (e.g., copper and zinc) that are initially leached from the illite and acidic fly ash.

The use of the zeolite or basic fly ash as a bottom layer minimizes the initial leaching of such pollutants as copper and zinc. This leaching is responsible for concentrations of 4 ppm copper and 1.7 ppm zinc in the initial 1.4 liter of effluent collected. The leaching occurs when only the illite and acidic fly ash combination is used in the lysimeter. However, when zeolite was used in combination with the illite and acidic fly ash, the above copper and zinc concentrations were reduced to 0.3 ppm and 0.6 ppm, respectively, in the initial 1.4 liter of effluent collected from the lysimeters (see Figure 2 and Figure 3). Basic fly ash, when used in combination with the illite and acidic fly ash, reduces the copper and zinc concentrations from 4 ppm and 1.7 ppm to 1 ppm and 0.6 ppm, respectively.

The results determined with the use of illite and acidic fly ash in the top layer of the laboratory lysimeters indicate that the sorbent combination of illite, followed by acidic fly ash and basic fly ash, in the weight ratios of 1:1: exhibits, in general, greater sorbent capacity than the sorbent combination of the acidic fly ash, illite and basic fly ash in the weight ratio of 1:1:1 (see Table 2). The sorbent capacity represents the amount of contaminant retained by the sorbent after the spent sorbent is extensively washed with water. However, with the exception of total cyanide, the sorbent removal capacity exhibited by the illite:acidic fly ash:zeolite (2:2:1) is the most effective of the combinations studied for treating all the measurable contaminants in the calcium fluoride sludge leachate followed by the illite, acidic and basic fly ashes (2:2:1) combinations.

The velocity of the leachate through the sorbent bed in the lysimeters also was found to influence the removal of the con-

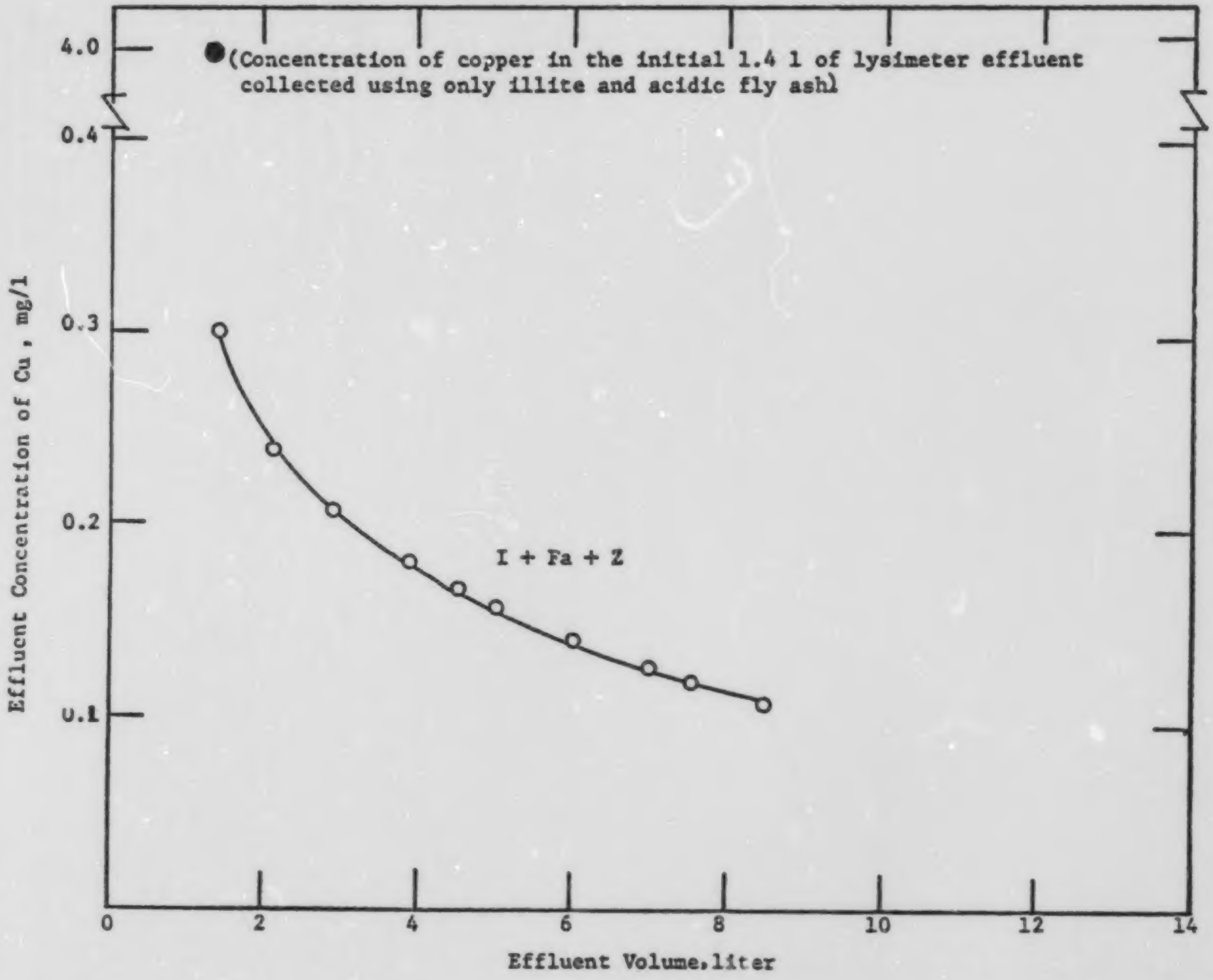

Figure 2 - Control of Copper Leaching from Illite and Acidic Fly Ash Using Zeolite

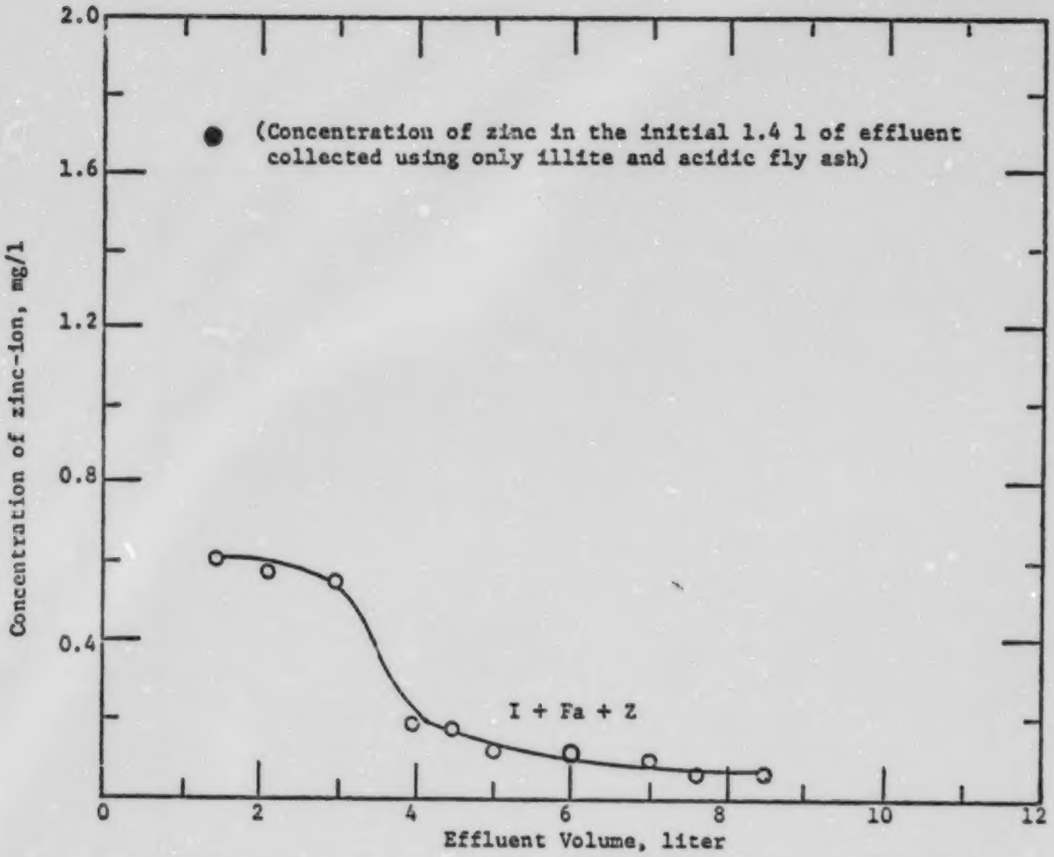

Figure 3 - Control of Zinc Leaching from Illite and Acidic Fly Ash Using Zeolite

taminants in the leachates. It does not effect the total amount of contaminant that can be removed by a sorbent (sorbent removal capacity) but it does define the volume of leachate that can be treated with maximum removal of a contaminant. For example, different leachate velocities were obtained when neutral calcium fluoride sludge leachate was passed through lysimeter that contained different amount of illite. The fluoride, and COD concentration in the effluent was monitored until breakthrough was achieved. The results are shown in Figure 4 and Figure 5. Here, it is seen that as the velocity of the leachate decreases, the volume of effluent that contains minimal amounts of fluoride and COD, increases.

The sorbent removal capacities, however, are not influenced by the velocity of the leachate through the sorbent bed. For example, the different velocities were found to have no significant effect on the sorbent removal capacity exhibited by the illite for fluoride and COD removals (see Table 3).

An examination of the curves in Figure 4 reveals that the optimum velocity for treating the largest volume of leachate with maximum fluoride removal should be less than 0.042 cm/min. The curve representing operation at the optimum leachate velocity should allow the greatest volume of leachate to be treated with a sharp rise in C/C_0 to breakthrough.

Pilot Studies

Since the combination of illite, acidic fly ash and zeolite (2:2:1) showed the most promise for treating the neutral calcium fluoride sludge leachate in the laboratory, two large vertical lysimeters were set up outdoors with sufficient sorbent to treat 140 gallons of neutral calcium fluo-

TABLE 2

REMOVAL CAPACITIES[1] OF COMBINED SORBENTS IN LYSIMETER FOR NEUTRAL CALCIUM FLUORIDE SLUDGE LEACHATE

Measured Parameters	Description	I+Fa+Fb 1:1:1	Fa+I+Fb 1:1:1	I+Fa+Fb 2:2:1	I+Fa+Z 2:2:1
Ca	Sorbent Capacity	0	0	0	406
Mg	Sorbent Capacity	849	528	515	866
Zn	Sorbent Capacity	5.9	7.2	6.1	9.5
F^-	Sorbent Capacity	110	105	128	148
Cn^-	Sorbent Capacity	1.3	1.5	3.9	1.7
COD	Sorbent Capacity	199	133	241	218

Remarks:

(1) Sorbent Capacities are expressed in g of contaminant removal per gram of sorbent used. I = Illite, Fa = Fly Ash (Acidic), Fb = Fly Ash (Basic), Z = Zeolite.

(2) Cd, Cr, Cu, Fe, Ni and Pb were analyzed and found to be below measurable levels.

ride leachate. The leachate was collected over a period of a year in order to study the effect of variations in the composition in the leachate on the removal process due to changes in plant operation. The pilot studies were designed for removal of fluoride present in the leachate down to 1 ppm or lower. The combination sorbent capacity for fluoride (see Table 2) defines the amount of total sorbent required in the lysimeters. The permeability of the clay fractions were adjusted by admixing with inert sand to obtain a leachate velocity of 0.01 cm/min through the sorbent bed in order to insure adequate removal of the fluoride ion. This leachate velocity was selected because it is 4 times smaller than the .042 cm/min which was shown earlier to approach the required leachate velocity needed to treat the largest volume of leachate with maximum removal of fluoride ion. The results of this study are shown in Figures 6 through 11.

The concentration of calcium in the three leachates that was passed through these lysimeters were 309, 115, and 228 mg/l (see Figure 6). The illite, acidic fly ash, zeolite combination (2:2:1) reduced these concentrations to effluent concentrations of approximately 80 mg/ℓ. During the addition of the initial leachate, poor removal of calcium was observed. This was probably due to channelling of the leachate through the sorbent as a consequence of adding the sorbent to the columns in the dry state rather than in slurry form. However, elimination of the channelling resulted in calcium concentration being rapidly reduced to 80 mg/l and was observed to be independent of influent concentration. For the case of copper treatment, the copper concentrations in the three leachates (0.12, 0 10, and 0.07 mg/l) were reduced to 0.04 mg/l (see Figure 7). Also, the leaching of copper from the illite and acidic fly ash (vide supra) is effectively controlled by the zeolite. The copper concentration in the effluent from the leachate initially treated was 0.08 mg/l, which is well below the influent concentration of 0.12 mg/l.

The effect of channelling on the copper removal can again be seen by the sudden rise in the effluent concentration after about 40 liters of leachate was treated. However, once the channelling was minimized, the copper concentration in the effluent was again reduced to 0.04 mg/l and observed to be independent of influent concentration. This channelling effect on removal points out the need for proper dispersion of the leachate stream through the bed.

The removal of magnesium by illite, acidic fly ash, zeolite combination (2:2:1) showed a dependency upon the influent concentration (see Figure 8). Influent magnesium concentrations of 29.6 mg/l, 75.2 mg/l

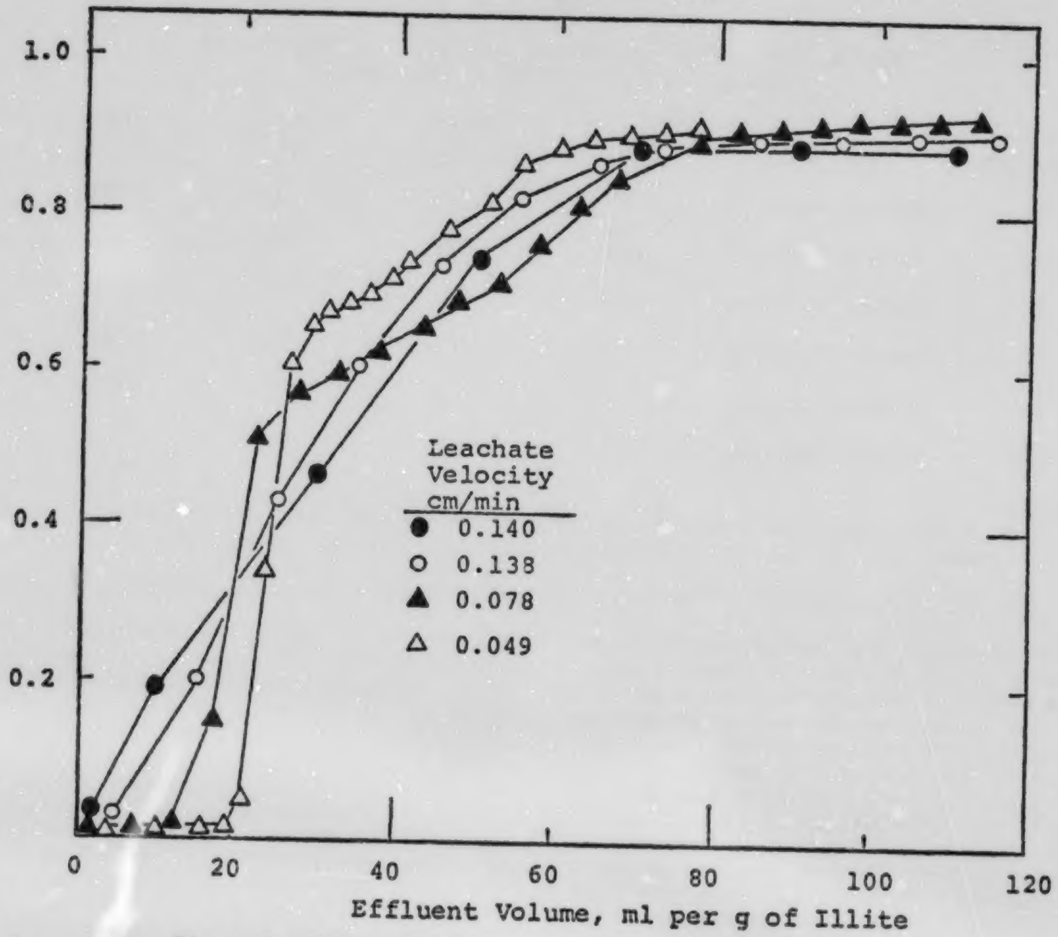

Figure 4 - Effect of Leachate Velocity on the Removal of Fluoride in Calcium Fluoride Sludge Leachate

TABLE 3

SORBENT CAPACITY EXHIBITED BY ILLITE FOR REMOVAL OF FLUORIDE AND COD AT DIFFERENT LEACHATE VELOCITIES THROUGH SORBENTS

Leachate Velocity Through the Bed (cm/min)	Sorbent Capacity for Fluoride μg/g	Sorbent Capacity for COD μg/g
.140	190	185
.138	186	192
.079	179	198
.042	175	216

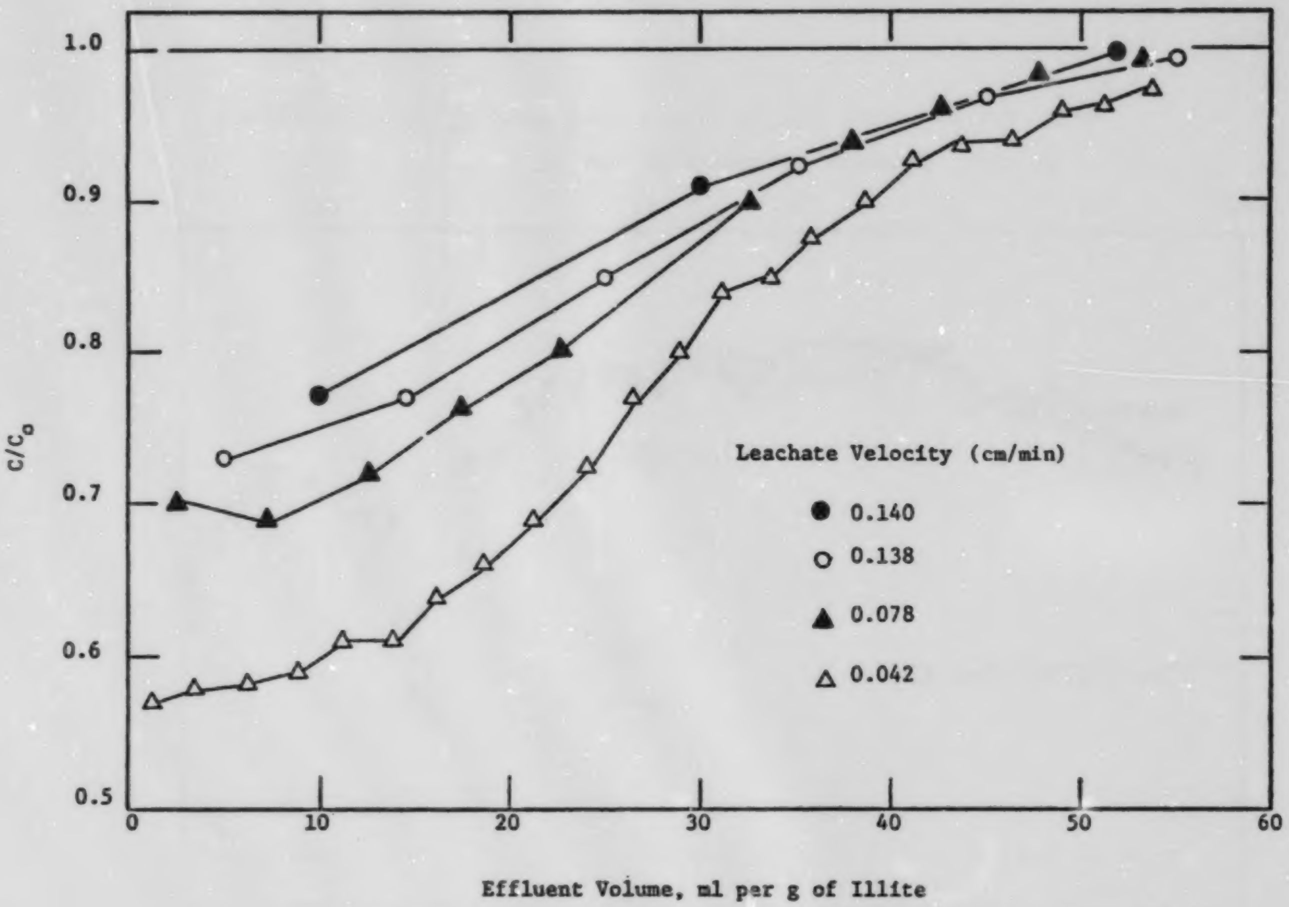

Figure 5 - Effect of Leachate Velocity on the Removal of COD in Calcium Fluoride Sludge Leachate

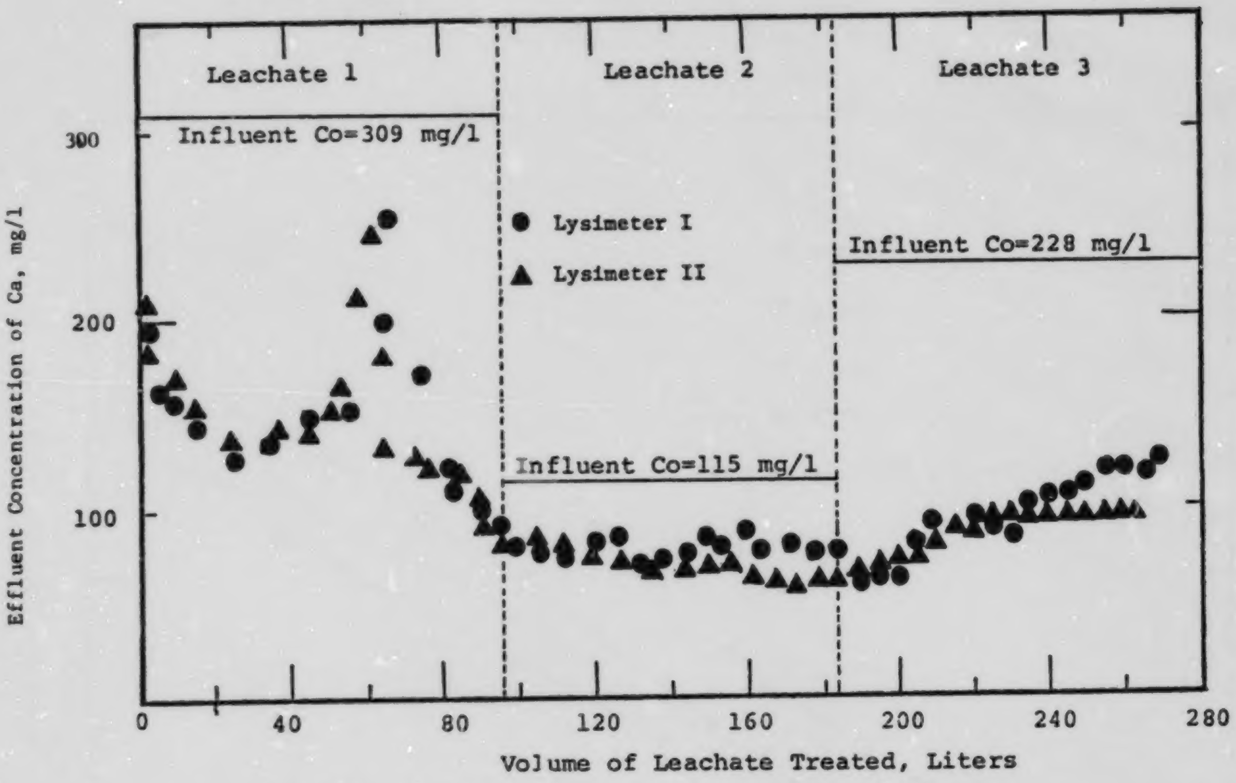

Figure 6 - Calcium Effluent Concentration in Pilot Scale Lysimeter Study

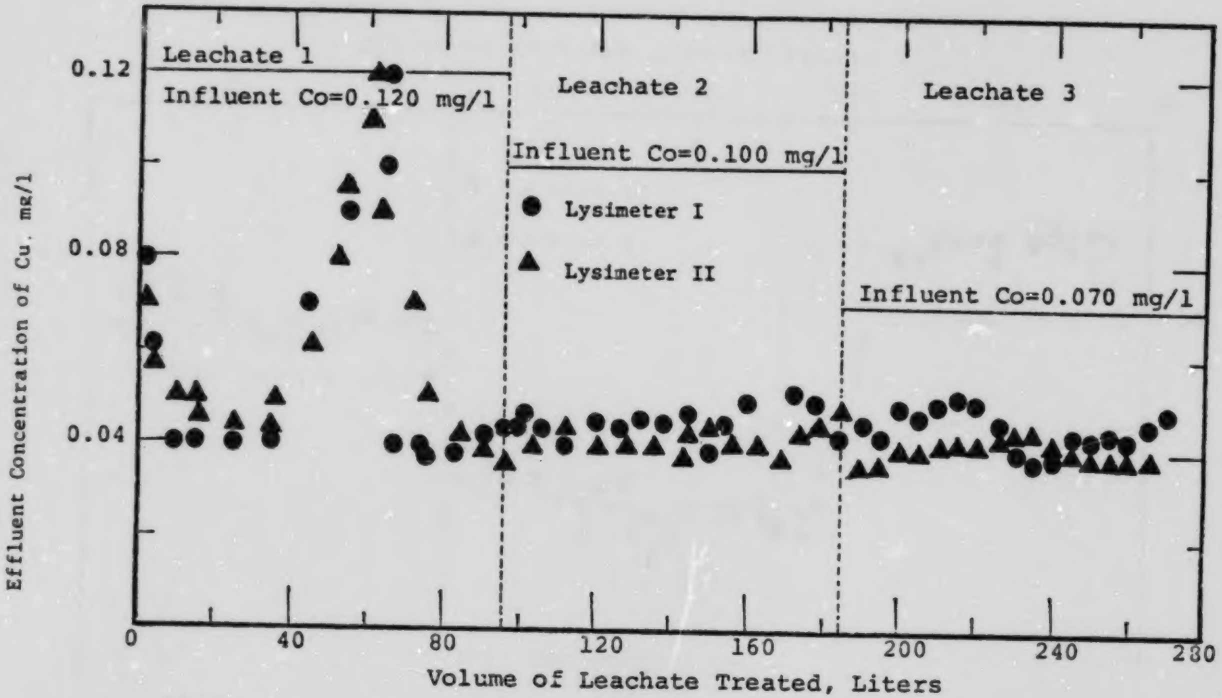

Figure 7 - Copper Effluent Concentration in Pilot Scale Lysimeter Study

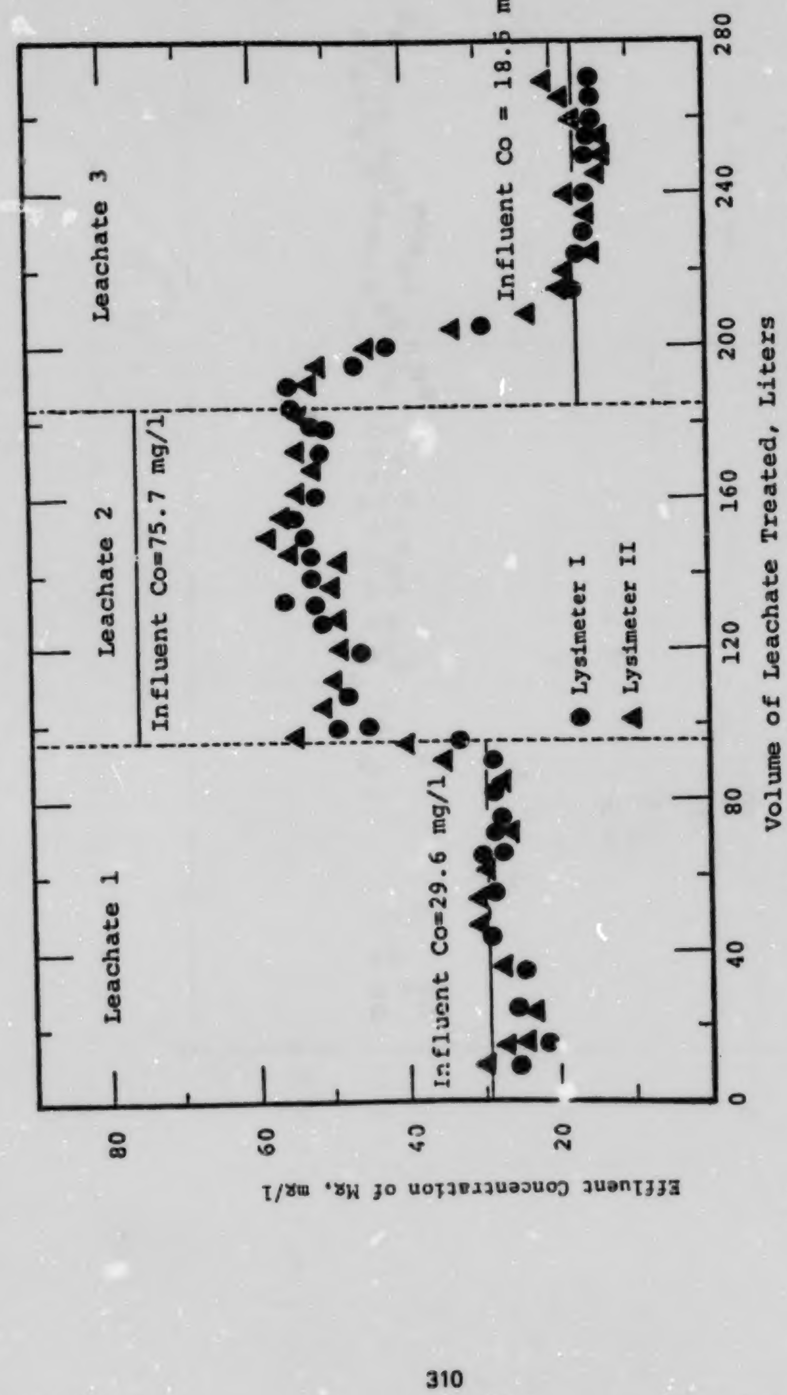

Figure 8 - Magnesium Effluent Concentration in Pilot Scale Lysimeter Study

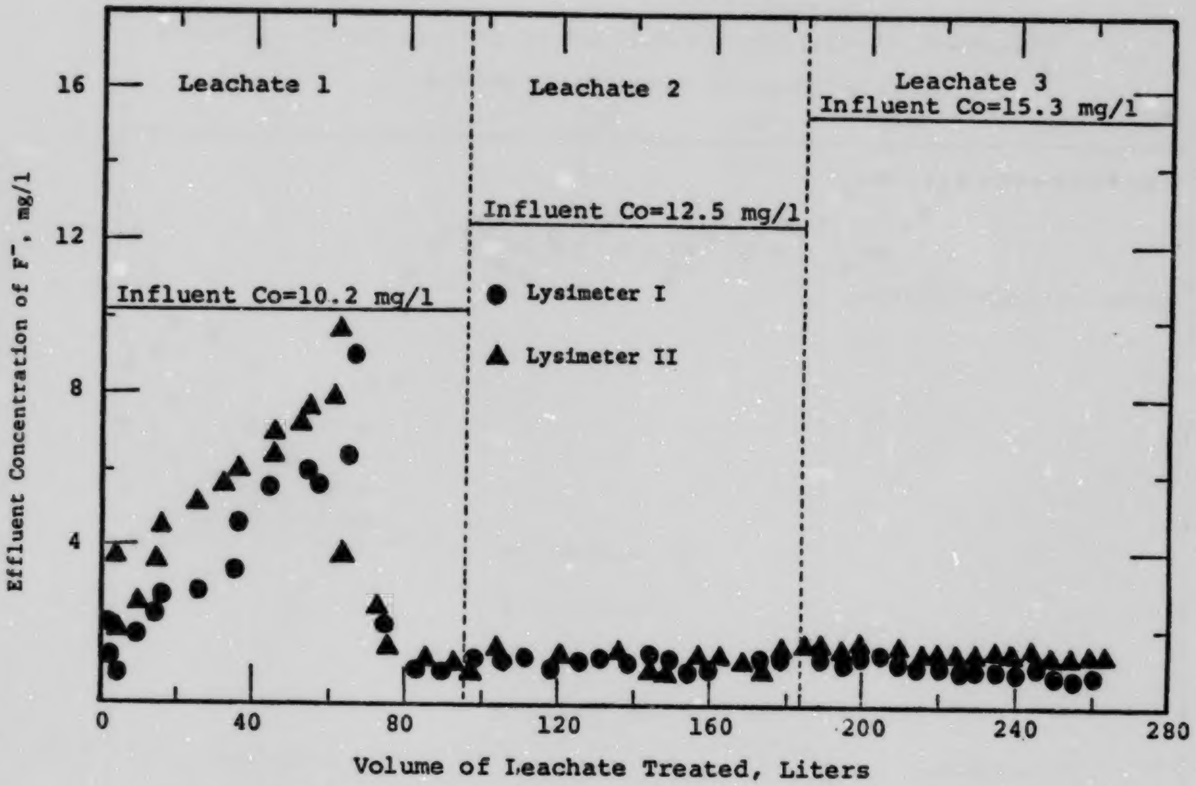

Figure 9 - Fluoride Effluent Concentration in Pilot Scale Lysimeter Study

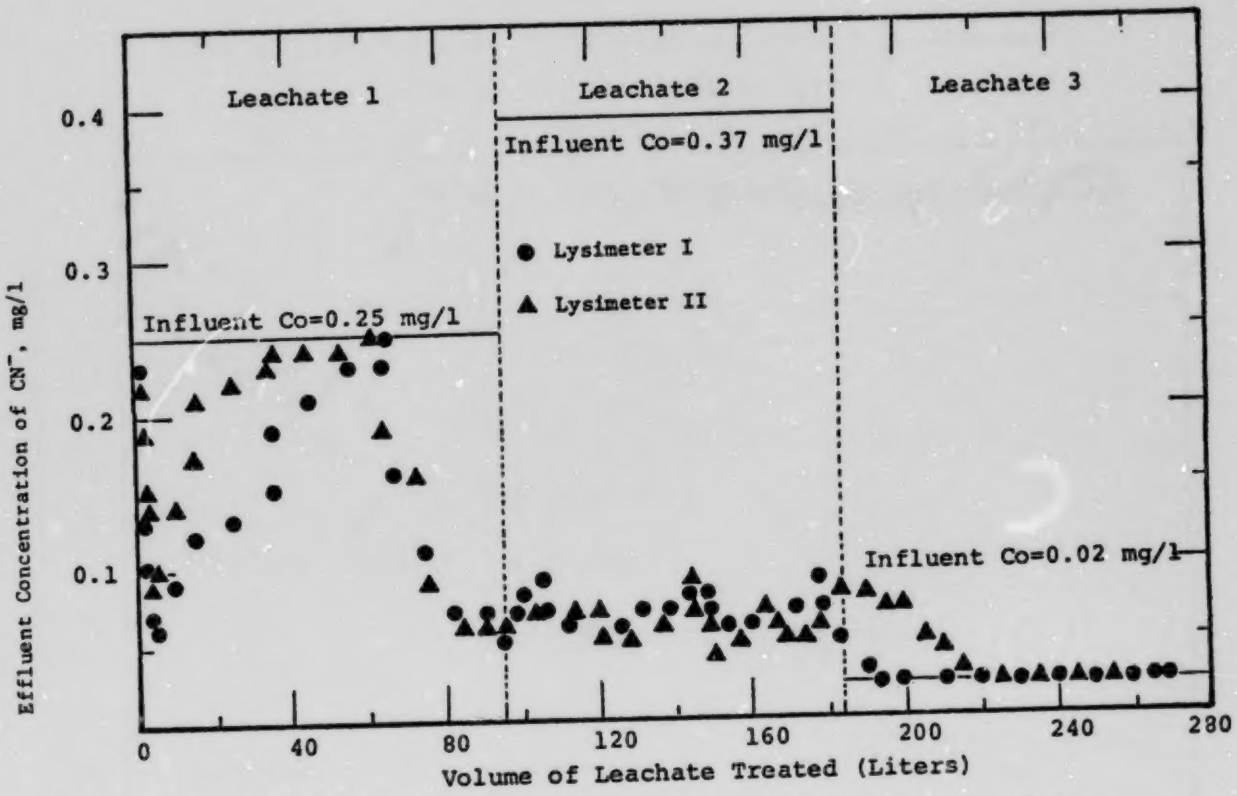

Figure 10 - Cyanide Effluent Concentration in Pilot Scale Lysimeter Study

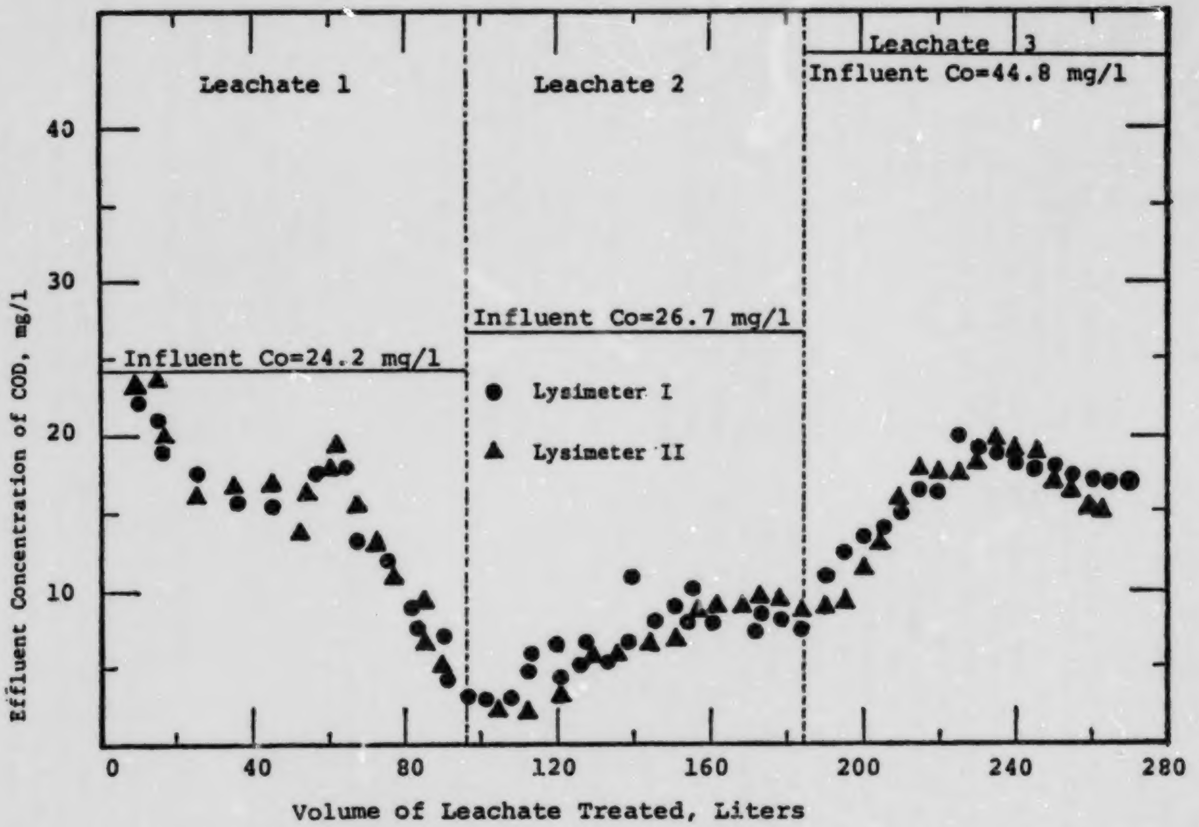

Figure 11 - COD Effluent Concentration in Pilot Scale Lysimeter Study

and 25.6 mg/l gave an effluent concentration of approximately 25 mg/l, 53 mg/l and 15 mg/l, respectively. One would expect results similar to that observed for the calcium and copper removals which appeared to be independent of the influent concentration. The explanation for these results is unclear at this time.

Not unexpectedly, effective removal of fluoride is also achieved with this sorbent combination since the amount of sorbent and the leachate velocity used were designed for fluoride removal. An effluent concentration of 1 mg/l was achieved with the influent concentration which varied from 10.2 mg/l to 15.3 mg/l (see Figure 9). Again, it is shown (as was the case for the calcium and copper results) that the concentration of fluoride ion in the treated leachate is independent of the influent concentration. This also appears to be true for the removal of the cyanide ion. Where the concentration of cyanide in the effluent is significant (i.e., 0.25 mg/l and 0.37 mg/l in the first two leachates) the sorbents reduce these concentrations to approximately 0.06 mg/l (see Figure 10). However, for the third leachate where the influent concentration was extremely low (0.02 mg/l), no significant removal of cyanide is observed. The minimum concentration to which the cyanide can be reduced to with this sorbent combination appears to be about 0.06 mg/l. However, if the illite, acidic fly ash and basic fly ash sorbent system (2:2:1) was used instead of the illite, acidic fly ash, zeolite combination (2:2:1), the effluent concentration of cyanide would probably be significantly lower than 0.06 mg/l. This is because of the greater sorbent removal capacity achieved with the non-zeolite combination (3.9 mg/gm) than with the zeolite combination (1.7 mg/gm) (see Table 2).

The minimum effluent concentration of the organics achieved with the illite, acidic fly ash, zeolite combination (2:2:1) appears to be dependent on the organic influent concentration. As the concentration of organics in the influent increases from 24.2 mg/l up to 44.8 mg/l, the concentration of organics remaining in the treated leachate also increases from a low of about 2.5 mg/l to 18 mg/l (see Figure 11). The reason for this behavior is not clear, but the overall results indicate that the illite, acidic fly ash and zeolite combination is not only extremely effective in removing the cations and anions, but also the organics present in the neutral calcium fluoride sludge leachate.

PROPOSED DESIGN OF A CALCIUM FLUORIDE SLUDGE LEACHATE TREATMENT SYSTEM

The results of the pilot study indicate that the use of the combination sorbent capacity (0.148 mg of fluoride removed per gram of sorbent used)(see Table 2), and a leachate velocity of 0.01 cm/min through the illite, acidic fly ash, zeolite combination (2:2:1) was effective in treating all the measurable constituents (i.e., Ca, Mg, Cu, F, CN and organics) in 140 gallons of leachate without breakthrough of any of the constituents occurring. In view of these results, two approaches are proposed for the treatment of leachate. This leachate will originate from a landfill (205' x 205' x 12') that is designed to contain an estimated 10 years production (27,400 tons) of calcium fluoride sludge. The 12 foot depth is presently being used in a storage pit at the plant where the sludge is generated.

The first approach (see Figure 12) will involve lining the sludge pit with an impermeable liner to prevent ground water intrusion. A 1 foot filter bed similar to that used in our pilot studies will be placed at the base of the landfill to remove the suspended solids. The leachate will be collected at the bottom of this filter bed and pumped on to an adjacent illite, acidic fly ahs, zeolite bed (2:2:1). The dimensions of this bed are 28' x 28' x 9'. The bed contains sufficient sorbent to treat one year's production of leachate at a rate of 7.5 l/min without ponding and still maintain a maximum leachate velocity through the bed of 0.01 cm/min. The 7.5 l/min flow rate was determined by assuming an annual average rainfall of 40 inches and that all the rainfall which falls upon the landfill becomes leachate.

The second approach is to line only the sides of the sludge pit with an impermeable liner to prevent the escape of leachate from the landfill and to place at the bottom of the landfill a 2 foot layer of the illite, acidic fly ash sorbent combination (2:2:1). This layer will be covered with a 1 foot layer of filter media to prevent clogging of the sorbent bed by the suspended solids in the leachate (see Figure 13). The 180' x 180' x 2' layer of sorbent combination would

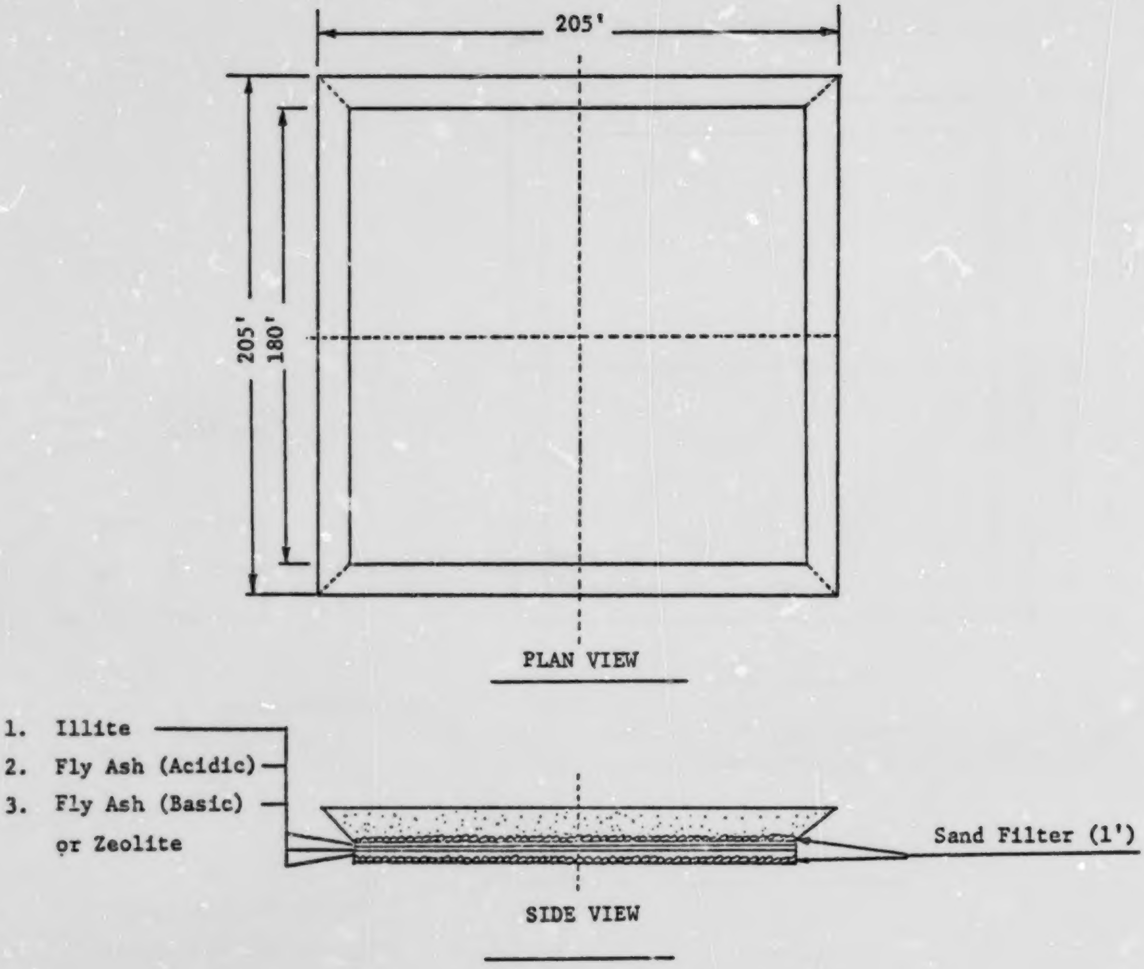

Figure 12 - Design of Sorbent Treatment System

be adequate to treat 10 years of leachate production containing on the average 10 mg/l of fluoride at the flow rate of 7.5 l/min. This approach, however, would be limited to areas where the ground water table is well below the landfill so that ground water intrusion through the sorbent bed into the landfill will not increase the rate of leachate production beyond 7.5 l/min.

The sorbent cost using the illite, acidic fly ash, zeolite combination (2:2:1) is estimated to be $1.37 per ton of calcium fluoride sludge disposed of in the landfill. A price of $10/ton for illite, and $50/ton for zeolite was used to estimate the sorbent cost. There is no cost associated with obtaining the acidic fly ash since it is a waste product and the utility is presently paying to have it hauled away.

Although the illite, acidic fly ash, basic fly ash sorbent combination (2:2:1) was not evaluated on the pilot scale (because of the time constraints), based upon the laboratory studies (see Table 2), this combination should also be effective for treating the measurable constituents (with the exception of calcium) in the calcium fluoride sludge leachate. The illite, acidic fly ash, basic fly ash combination offers a far less expensive approach. If the calcium ion concentration encountered in this leachate (see Figure 6) presents no significant problem and its attenuation not considered, the sorbent cost for disposing

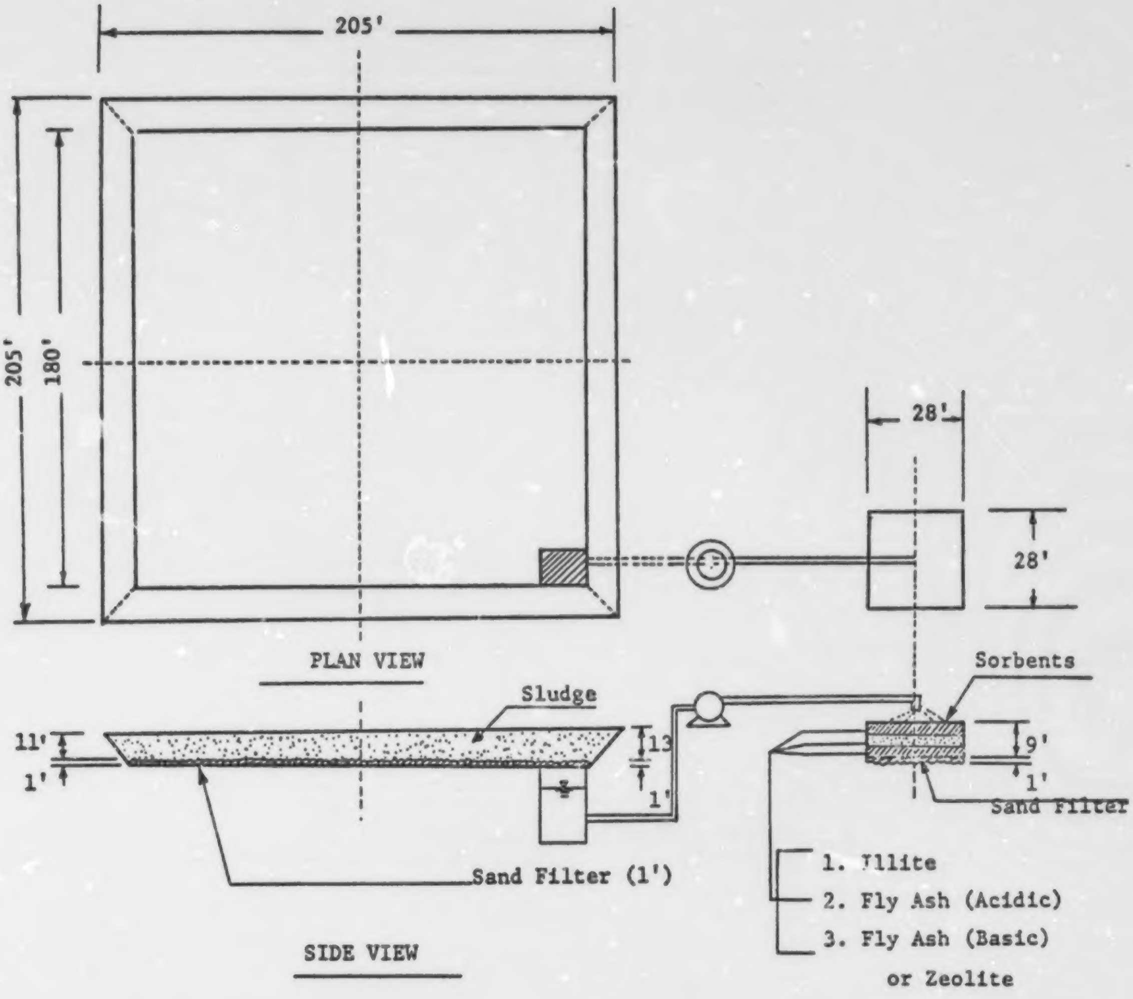
205'
205'
180'
28'
28'
PLAN VIEW
Sludge
Sorbents
11'
1'
13'
1'
9'
1'
Sand Filter
Sand Filter (1')
1. Illite
2. Fly Ash (Acidic)
3. Fly Ash (Basic)
or Zeolite
SIDE VIEW

Figure 13 - Design of Liner Bed

of 1 ton of calcium fluoride sludge decreases to $0.45. All bed or layer dimensions remain the same. It should be noted that there is a disadvantage at the present time to using the illite, acidic fly ash, basic fly ash combination rather than the illite, acidic fly ash, zeolite combination. The supply of basic fly ash from the utility at which it is generated is somewhat limited. The power station generates more acidic fly ash than basic fly ash.

CONCLUSIONS

As a result of these studies, an extremely promising inexpensive system has been developed for the treatment of leachate arising from calcium fluoride sludge disposed of in a landfill. The combination of illite, acidic fly ash and zeolite or illite, acidic and basic fly ashes has been found to be the most effective in a layered system for removing cations, anions and organics in neutral calcium fluoride sludge leachate.

The order that the natural clays and fly ashes are used in a layered bed influences the removal of the cations, anions and organics in the industrial sludge leachates. Acidic sorbents (e.g., illite and acidic fly ash), which can initially induce slightly acidic conditions into the leachate, are placed at the top of the layered system followed by those sorbents which can induce slightly alkaline conditions in the leachate. This results in the removal of the anions before the cations.

Alkaline conditions at the base of the bed are desirable. This favors the removal of both the cations in the leachate and the heavy metal cations initially leached from specific sorbents (i.e., illite and acidic fly ash). Either zeolite or basic fly ash was found effective in controlling this initial leaching of heavy metal ions by the acidic sorbents.

In the design of a sorbent system, the total amount of a specific cation, anion or organics which is removed by a sorbent is indicated by the sorbent removal capacity. The volume of leachate that can be treated with maximum removal is regulated by the velocity of leachate through the sorbent bed. This leachate velocity can be regulated by sorbent bed height which defines leachate volumetric flow rate through sorbent bed, under specified hydraulic conditions. These hydraulic conditions can be controlled by varying the amount of inert material added to the clays to regulate their permeability, or varying the particle size of the sorbents in the bed.

With the exception of magnesium, the illite, acidic fly ash, zeolite sorbent combination in the weight ratio of 2:2:1 was found to be effective for treating the measurable contaminants in calcium fluoride sludge leachate on a pilot scale. A calcium ion concentration of over 300 mg/l in leachate was reduced to 80 mg/l, copper ion concentration of 0.12 mg/l was reduced to 0.04 mg/l, the fluoride ion concentrations were reduced from 15 mg/l to 1 mg/l, the total cyanide was reduced from 0.37 mg/l down to about 0.06 mg/l and the COD was reduced from about 45 mg/l down to 15 mg/l. Magnesium ion concentration was reduced from 76 mg/l down to only about 53 mg/l. In addition, with the exception of the magnesium and the COD, the resultant effluent concentrations were found to be independent of influent concentrations.

Sorbent cost for the illite:acidic fly ash:zeolite combination (in the weight ratio of 2:2:1) required for the treatment of the leachate during a ten year period of working the landfill has been estimated to be $1.37 per ton of sludge disposed of in the landfill. This cost is based upon an annual rainfall of 40 inches, assuming that all the rainfall that falls upon the landfill becomes leachate. However, this cost may be reduced to only $0.45 per ton of sludge disposed of in the landfill if the illite:acidic fly ash:basic fly ash combination (in the weight ratio of 2:2:1) is used. Based upon the laboratory lysimeter results, the illite:acidic fly ash:basic fly ash combination appears promising for the treatment of the measurable contaminants (with the exception of the calcium ion in the calcium fluoride sludge leachate).

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SELECTION OF COVER FOR SOLID WASTE

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ABSTRACT

Selection and design of cover for solid/hazardous waste can be accomplished effectively by engineering planning in four steps. First, identify the functions to be served by the cover and establish relative importances, e.g., impeding water percolation is more important than supporting vegetation, etc. Second, use data on soil properties in terms of the Unified Soil Classification system or the U. S. Department of Agriculture system to rate available soil for effectiveness in the various functions. Third, specify certain design procedures in the disposal operation, including those necessary for circumventing the deficiencies of the selected cover soil. Placement procedures such as compaction will improve the soil for certain functions. Elsewhere, the soil properties favorable for one function are unfavorable for another, e.g., a clayey cover soil impeding water percolation will prevent escape of decomposition gases that may also be desired. Fourth, where a single soil cannot serve contrasting cover functions, incorporate features such as layering or use special nonsoil materials and additives.

INTRODUCTION

This paper summarizes the first phase of a study on cover for solid and hazardous waste.(1) The most common cover material has been soil, particularly indigenous soil at the disposal site. This is not to say, however, that other materials cannot be used, and quite likely synthetic and waste materials will be used in greater amounts in the future. Although some aspects of soil as cover have not been thoroughly investigated, much is standardized and well known from previous experience and practice in soil mechanics, agriculture, and soils construction.

BACKGROUND

Preliminary investigations for solid waste disposal operations are summarized briefly here, whereas a review of all aspects of solid waste disposal is available elsewhere.(2) During preliminary investigations the potential sites are chosen, the local geology is determined, and the subsurface is explored. Subsurface exploration may be accomplished by trenching or boring, and soil samples are usually obtained for laboratory testing.

One purpose of preliminary site investigations is to ascertain the subsurface conditions of each potential site. The geology should primarily be favorable to minimizing the environmental impact of the disposal project on surrounding water supplies, i.e., not significantly altering water quality. Subsurface exploration should provide soil samples representative of the soil types and stratification. After boring logs have been prepared and the soils classified, a specific site is ordinarily selected on the basis of the type of waste disposal area, suitable topography, favorable geological and groundwater conditions, and availability of adequate amounts of cover soils/materials with necessary properties for minimizing objectionable environmental effects.

Geologic and subsurface sampling and exploration may also be conducted on potential off-site borrow areas, which might provide suitable soil for cover. Investigations should be sufficient to define the soil types and quantities and natural water contents. Laboratory studies may also include tests for classification and compaction and, if necessary, for permeability and strength properties in compacted samples.

SOIL CLASSIFICATION

Currently, soils used in solid waste disposal design and construction are classified according to either the Unified Soil Classification System (USCS) or the U. S. Department of Agriculture (USDA) system. The USCS is engineering oriented; soils are grouped according to gradation of particle sizes, to percentages of gravel, sand, and fines, and to plasticity characteristics. The USDA system classifies on the basis of texture only, i.e., percentages of gravel, sand, silt, and clay. Figure 1 presents relationships between the two systems based on laboratory tests on hundreds of soil samples.

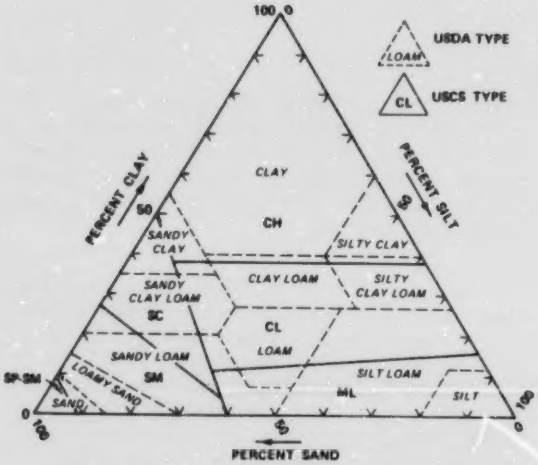

Figure 1. USCS superimposed on USDA soil chart.(3)

REQUIREMENTS OF COVER ON SOLID WASTE

A basic legal requirement in solid waste disposal is that a layer of earth be placed over the compacted solid waste after each day's operation. Most solid waste disposal operations also employ a final, thick soil layer for long-range cover after completion of the operation. A membrane or other synthetic material is sometimes used in place of soil. Intermediate covers are also distinguished for surfaces exposed for long periods but eventually buried under subsequent lifts.

COVER FUNCTIONS

Specific functions of cover on solid and hazardous waste sites are as follows:

a. Control insect emergence and entrance.
b. Control rodent burrowing.
c. Reduce bird and animal attractiveness.
d. Minimize or maximize water percolation.
e. Minimize water erosion.
f. Minimize or maximize gas movement.
g. Minimize fire hazard potential.
h. Minimize blowing paper.
i. Control noxious odors.
j. Provide sightly appearance.
k. Minimize settlement and maximize compaction.
l. Provide for vegetative growth.
m. Minimize wind erosion and dust generation.
n. Resist cold climate deterioration and operational difficulties.
o. Preserve slope stability.
p. Resist cracking.

Functions k and m concerning trafficability and wind erosion are discussed later, in examples of the technical approach.

Among these functions, a few stand out as primary while the others are usually secondary. Primary functions are more or less independent and concern such landfill processes as movement of water and gas and susceptibility to erosion. Secondary functions restate primary functions viewed in a different sense. Resistance to fire, a secondary function, is contingent upon satisfactorily impeding air or gas migration, a primary function. Similarly, slope drainage (and side slope stability) is a secondary or somewhat different way of looking at the primary function, assisting water percolation. Physical characteristics of the cover that are basic to the primary cover functions and are also involved in most of the secondary functions are conductivity to water, conductivity to gas, shear strength, and tensile strength (or capillary potential).

FUNCTIONAL PRIORITIES

The functions as listed above are straightforward, but in actuality cover functions are complexly interrelated; for this reason, designing solid waste cover involves considerable subjective judgment. Ranking of priorities is necessary in determining which functions are most important at the specific site and in designing features to compensate for adverse side effects on other cover functions. For example, a cover that functions to impede infiltration and percolation of water from the surface will also impede upward movement of decomposition gases. If gases are to be moved through the cover to minimize lateral movement, a gas vent system may be required. A brief hypothetical scenario illustrates the problem of conflicting functions and suggests the priorities approach recommended here.

Suppose that it has been determined that cover for a disposal area receiving hazardous chemicals must not only serve all of the usual functions but have special effectiveness in preventing the generation of dust in a region prone to high wind velocity. Suppose that the powdery waste is damp upon arrival at the area but that it dries quickly in the semiarid climate. Finally, suppose that the area is usually subjected to a two-month rainy season in which much of the 15-in. annual precipitation is concentrated.

First priorities for most of the year would be wind erosion resistance and dust control with water infiltration control and other functions following in progressively lower rankings; this is assuming that there are no other particular hazards, such as flammability or generation of toxic gas. Control of animals and asthetic considerations usually fall low in the ranking because they are insensitive to choice of soil type. The problem of air pollution by toxic dust particles is solved by specifying that the daily cover shall consist of sand, which by its coarse grain size will resist wind erosion, and shall be 8 in. or more in thickness to assure complete shielding of an irregular surface of waste. The infiltration of rainwater largely takes place in the short rainy season; therefore, specifications should require that all intermediate cover exposed during this rainy period shall include a 6-in. layer of compacted clay below 6 in. of sand. Finally, it may be specified that certain dust palliatives or water be applied during disposal operations to prevent drying and dust generation by traffic erosion.

SELECTION OF COVER SOIL

DETERMINING COVER FUNCTIONS

The ranking of cover function priorities is a key part of the cover selection procedure, but it can only be accomplished site specifically. For example, at many landfills the rate of infiltration of surface water may be of utmost importance; elsewhere, for instance in arid regions, minimization of infiltration and percolation is entirely subordinate. Long- and short-term functions should be separated and given some absolute ranking. For example, it may be difficult to distinguish the relative importance of reduction in dust during the operation of a landfill as opposed to the reduction of potential for spontaneous combustion, where the latter requires covering and enclosing cells in clay-rich, but dust-prone, soil. These decisions are made at the design stage. Only at this point in the development of a project can the actual conditions, such as climate, soil availability, transportation costs, and population proximity, be evaluated in the context of generalizations such as made below.

For each function judged to be significant, soils should be ranked from best to worst, e.g., for trafficability and wind erosion in Table 1. Next, it will be necessary to flag those soils that are actually available for use at the site. These may include materials brought in from a distance in preference to indigenous soil. Allowance may be needed for the high cost of importing materials.

RATING SOILS

Soils can be rated from I (best) to as many as IX or more (poorest); examples are shown in Table 1. Quantitative parameters are also provided in the table so that the reader can see the absolute position of a

TABLE 1. EXAMPLE SOILS RANKING FOR FUNCTIONAL PERFORMANCE

USCS Soil	Description	Ranking For Trafficability (RCI Value)	Ranking For Wind Erosion (% Sand/Gravel)
GW, GP	Gravel	I (>200)	I (95-100)
GM	Silty Gravel	III (177)	III (60-95)
GC	Clayey Gravel	V (150)	V (50-90)
SW, SP	Sand	I (>200)	II (95-100)
SM	Silty Sand	II (179)	IV (60-95)
SC	Clayey Sand	IV (157)	VI (50-90)
ML	Silt	IX (104)	VII (0-60)
CL	Silty Clay	VII (111)	VIII (0-55)
MH	Clayey Silt	VIII (107)	IX (0-50)
CH	Clay	VI (145)	X (0-50)

particular soil rating. The first column concerns the go/no go aspect of trafficability that may be particularly critical during disposal and covering operations. The ratings of I to IX from coarse granular to fine silty soils are based on a complete set of rating cone index (RCI) values. The second data column concerns wind erosion control, and soils are rated I to X according to their sand and gravel content. The basis for the ratings and quantitative parameters (Table 1) is reviewed in the next two sections.

EXAMPLE FUNCTION - TRAFFICABILITY

Trafficability of solid waste cover is the capacity of the material to support vehicle traffic. Factors influencing trafficability of cover soils include not only the many variables that combine to determine the strength but also the slope, condition of underlying solid waste, and geometrical obstacles, such as drainage ditches. Trafficability of a soil is considered adequate for a given vehicle if the soil has sufficient bearing capacity to support the vehicle and sufficient traction capacity to enable the vehicle to develop the forward thrust necessary to overcome its rolling resistance.

MEASURING SOIL TRAFFICABILITY

It has been demonstrated in military studies (3) that the go/no go performance of vehicles can be predicted with reasonable accuracy using soil strength indexes. Relative shear strength of soil may be evaluated with a cone penetrometer. This instrument employs a 30-deg cone with 1/2-sq-in. base-end area. The force necessary to push the cone slowly through the soil is indicated as the cone index (CI), from 0 to 300. The value 300 occurs under a force of 150 lb.

As traffic crosses moist or wet soil, the soil is remolded and its strength usually is changed. Remolding index (RI) procedures quantify this change. Five CI values are read at 1-in. increments to a depth of 4 in. in undisturbed soil, and five CI values are obtained in the same soil after remolding. The RI is determined by dividing the sum of the CI readings made after remolding by the sum of the readings made before remolding.

The rating cone index, defined RCI = CI x RI where CI is measured undisturbed in the field, expresses the probable strength of the specific soil under repeated traffic. Figure 2 shows the RCI for the various soil types determined in a large testing program. Comparing the relationships for RI and RCI, it can be seen that the CI for more or less undisturbed soil cancels and the RCI largely represents the trafficability strength of remolded soil. Accordingly, the RCI is directly applicable to solid waste cover where the soil is always in a remolded condition. For coarse-grained soils or clean sands, CI measurements alone are usually adequate to quantify trafficability.

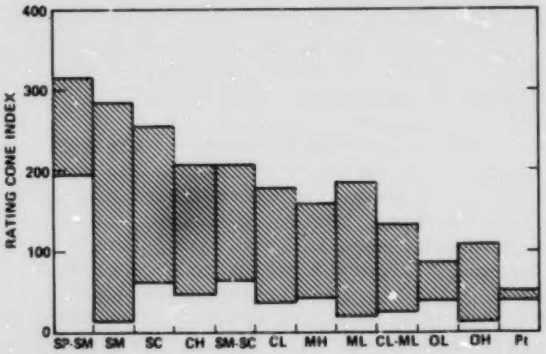

Figure 2. RCI ranges for USCS soil types.(3)

EVALUATING TRAFFICABILITY

The minimum RCI, just sufficient for 50 passes of a specific vehicle, is called the vehicle cone index (VCI). If the soil RCI is higher than the VCI of a particular vehicle, numerous successful passes can be expected along the same straight path, or one such vehicle can be expected to execute severe maneuvers without becoming immobilized. The VCI for individual vehicles within broad categories are given in Table 2. Categories 2 through 7 include vehicles commonly used in waste disposal operations.

TABLE 2. VCI FOR VEHICLE CATEGORIES

Category	Vehicle Type	VCI Range
1	---	20-29
2	Tractors with low contact pressure	30-49
3	Tractors with medium contact pressure	50-59
4	Tractors with high contact pressure	60-69
5	All-wheel-drive trucks	70-79
6	All-wheel- and rear-wheel-drive trucks	80-99
7	Rear-wheel-drive road trucks	100 or greater

SPECIAL OPERATING PROCEDURES

In cases where cover trafficability is marginal or where modifications producing beneficial trafficability effects are not compatible with other cover functions, special design procedures may be followed. Four procedures are recommended.

Semipermanent Distribution Routes

Lay out the on-site handling and covering operation so that vehicles with potential trafficability problems are confined to limited paths designed and maintained for good trafficability. Indigenous or imported granular soils, base courses, and/or inexpensive pavements should be considered to prepare a distribution route for use during the operations at one level, for example.

Daily Maintenance

Daily maintenance may be established and equipment made available to assure that deterioration in cover trafficability is rectified before becoming disruptive. As a first approach, it may be effective to assign municipal road grading equipment and a crew to half-day maintenance periods at intervals of two to five days to add supplemental soil, then sprinkle, smooth, and compact. The on-the-site equipment should be sufficient to take care of rutting and other trafficability problems that arise during daily operation. Stockpiles of suitable additive material (granular, clayey, etc.) should be kept on hand or be readily available.

Special Wet-season Area

Organize the disposal area in such a way as to have a standby section available for use during periods of inclement weather. This section might be laid out on well-drained sandy terrain near arterial access and be composed of single-height waste cells where likelihood of trafficability problems is minimal.

Special Waste Compaction

It is anticipated that cover trafficability may become a problem where high degrees of compaction of solid waste are not achieved. Deep, immobilizing ruts may develop as a consequence of spongy waste subgrade rather than deficiencies of the cover soil. Attempts to reduce this problem may be made by increasing the ratio of soil to waste in the covering operation. Improving compaction of waste should help, and in the extreme, bailing of the solid waste might be considered.

EXAMPLE FUNCTION - WIND EROSION CONTROL

This section follows a procedure(4) for using wind characteristics along with soil and vegetation factors to predict soil loss and as a basis for selecting and designing cover to control wind erosion. Most studies on wind erosion and measures for its reduction have been conducted in the interest of agriculture where the seriousness on a regional scale is obvious. Corresponding erosion potential at solid waste sites is of much lesser magnitude, but another aspect of concern arises where the soil is actually breached by erosion to expose the waste to potential wind dispersion.

WIND EROSION EQUATION

Soil loss depends on cloddiness, surface roughness, and surface moisture of the soil; on amount, kind, and orientation of the vegetation; on wind velocity or force; and on the windward distance across the field. The wind erosion equation (WEE) expresses functionally the amount of erosion in tons per acre per annum, from a given soil surface as $A' = f(K', C', L', T', V')$ where K' = soil erodibility index; C' = climatic factor; L' = field length along prevailing wind erosion direction; T' = soil ridge roughness factor; and V' = equivalent quantity of vegetative cover.

The WEE is potentially useful for determining acceptability or unacceptability of a solid waste cover design where coupled with a criterion for permissible levels of annual soil erosion. Ways of reducing high erosion should become apparent when each factor in the equation is carefully considered separately; thus, a manipulation of the orientation of a landfill might reduce L' and, in turn, erosion loss. This and other methods of design modification are discussed below.

DESIGNING WIND EROSION CONTROL

Design for wind erosion control at solid waste sites has considerable flexibility in comparison with control measures applicable to agricultural fields. Each factor of the WEE including even C' concerns one or more variables that are at least locally subject to manipulation. Techniques for designing new sites or modifying existing ones are briefly explained below.

Soil Composition

The susceptibility of soils to wind erosion is a function of the coarse soil fraction. Figure 3 gives erosion loss values corresponding to measured percentages of grains over 0.84 mm in diameter (for level terrain). The figure is a basic tool to be used in design for selecting or modifying cover soil type on the basis of sieve analyses of those soils available.

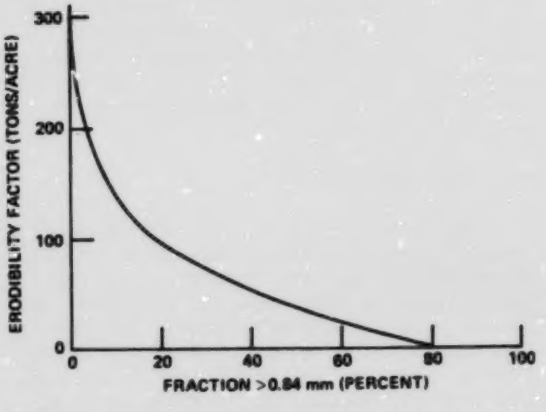

Figure 3. Wind erosion versus percent coarse fraction.(4)

Knoll and Side Slope Configuration

The vulnerability of knoll-like configurations on cover can be evaluated with a factor (Figure 4) that adjusts erosion loss percentage by 100 or more in comparison with erosion loss from a similar flat surface. This factor should be used to estimate the effects of sloping sides of landfills facing toward the prevailing winds. Figure 4 shows that even gentle windward slopes may cause major erosion concentration and, therefore, are places in need of stabilization or protection (with wind barriers). Thus, it may be reasonable to arrange side slopes in protected orientation and lee side positions.

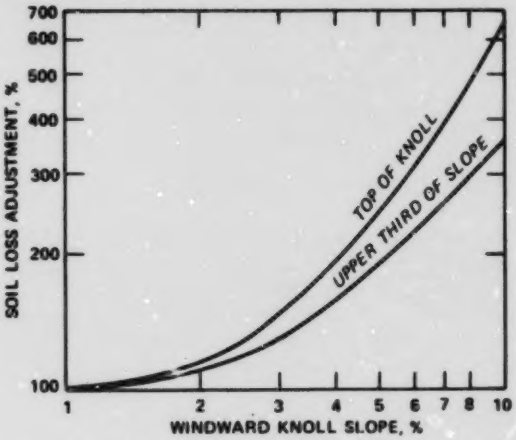

Figure 4. Knoll adjustment in percent.(5)

Length-width and Orientation Configuration

L' is an important variable in the wind erosion process. On an eroding surface, the rate of soil flow is zero on the windward edge and increases with leeward distance until, on a large surface, the flow reaches a maximum. Three techniques available during the designing of a landfill to reduce L' and soil loss are: orient width parallel to prevailing wind; use barriers at strategic locations; and use only a small segment of landfill at one time, keeping the remainder protected by vegetation or other means.

Vegetation Cover

The importance of healthy vegetation in reducing wind erosion can hardly be overemphasized. Even the relatively sparse cover provided by crop stubble has a significant effect in the WEE. Timely seeding and emergence of vegetation are important in reducing bare soil exposure time. However, timing may not be a straightforward matter since coordination with the growing season, windy season, and disposal operations plan must also be assured.

Additives

Since the need for wind erosion protection at landfills is often short-term and may be urgent, emergency methods should be such as can be applied when the need arises and will be instantaneously beneficial. The application of chemicals to soil cover is one of the most effective quick-response methods for stabilization. Common soil stabilizers fall into five broad groups:(6) inorganic salts, inorganic cementing materials, bituminous materials, resinous materials, and polymeric materials. Actually, the increasing of soil moisture by sprinkling with water is temporarily quite effective. Unfortunately, wind erosion is most common in water-deficient areas where, in addition, evaporation rates are usually high.

FUTURE DIRECTION OF STUDY

The second phase of this study is proceeding in the following directions:

a. Revising and refining the interim report,(1) particularly for operational practicability.

b. Establishing comprehensive design and construction techniques applicable after soil selection.

c. Providing for analysis of percolation through cover to allow for estimating leachate production and for designing effectively in that usually high-priority function.

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LABORATORY ASSESSMENT OF FIXATION AND ENCAPSULATION PROCESSES FOR ARSENIC-LADEN WASTES

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ABSTRACT

This study is evaluating the effectiveness of several proprietary and generic processes for the fixation of arsenic in arsenic bearing wastes. Three industrial solid wastes that are high in arsenic conentration have been treated by generic processes in the laboratory and by proprietary processes at vendor's facilities. Leaching studies on the treated wastes are being performed to assess the relative safety of each product for disposal. Data are presented from shake tests on pulverized samples and on intact monolithic samples. Leachate analyses have shown that some processes have value, but that great differences exist among the various processes.

INTRODUCTION

Many industrial residues containing arsenic are presently held in long term storage because of the lack of an acceptable disposal method. Other similar residues are disposed of on land, but the design, construction, and operation of sites that can protect water resources from arsenic contamination are often very difficult and expensive. Several regions of the country do not contain many sites with the needed hydrogeological characteristics, so hauling becomes a major expense. Long-distance hauling of hazardous wastes also incurs the risks of accidental spills.

For these reasons, a study is being conducted to learn if ways exist or can be developed that can make arsenic-laden residues safe for disposal at sites less restricted than the types of sites presently required.

A national survey of industrial users and producers of arsenic-containing materials indicated that three forms of arsenic-bearing wastes should be of primary concern because of their amount in storage (or amount annually produced) and their arsenic concentration. These wastes are:

(1) Residues from the manufacture of organic arsenical herbicides. Most of these wastes are presently stored at or near the facilities producing them.

(2) Filter cake from the production of food-grade phosphoric acid. Most of these wastes are presently shipped to secured landfills.

(3) Flue dusts from nonferrous smelting operations. A variety of disposal, storage, and recycling routes is presently employed by the many facilities producing these residuals.

Waste No. 1 is composed mostly of sulfate and chloride salts. It contains approximately 2% organic arsenicals, or 0.9 to 1.0% expressed as As. Waste No. 2 is a yellow, damp (37% moisture) acidic filter cake. It contains approximately 1.2% As_2S_3, or 0.7% expressed as As. Waste No. 3 as used in this study was a fine white powder containing 90% As_2O_3, or 68% expressed as As. Although most flue dusts are much lower in arsenic content, As_2O_3 is the major arsenic compound in all of them, so this material was selected to represent flue dusts. The arsenic concentrations stated here are those provided by the sources of the wastes, and they have been confirmed by digests and analyses of the actual waste samples used in this project.

Each of these wastes has been treated with fixation processes by commercial or academic developers of those processes. In addition, generic processes such as formation of less soluble compounds and mixing with Portland cement have been developed in the laboratory. For specific wastes of the types addressed here, it is quite possible that an ad hoc fixation process may be more successful than commercial processes, which are developed and offered for a broad spectrum of wastes ranging from radioactive liquids to flue gas desulfurization sludges. Leaching tests have been used to evaluate the success of each fixation attempt.

The term "fixation" is used throughout this paper to describe any process or effect that is intended to, or actually does, reduce the leaching of arsenic from treated residues.

This paper presents information on the fixation of all three wastes involved in the study. Products of five vendor processes are discussed, representing a wide range of approaches to fixation. All products discussed here are solid and monolithic; none are granular.

METHODS

The three wastes as described above were each subjected to five processes. A coding system for each product is used here; for example, in the product identified C155,

C designates the commercially available process
1 indicates Waste No. 1
55 indicates that the waste loading, or percentage of waste in the fixed product, was 55%. All waste loadings and other percentages in this paper are expressed on a wet weight basis.

Two types of leaching tests were used: an elutriate test and a slow shake test. The elutriate test, modified from that developed for assessing dredged materials(1), was as follows in this brief summary:

(a) Crush the waste product and screen through #10 sieve. Use 100 gm of material that passes the screen.

(b) Mix the granular material from (a) with 1 ℓ of CO_2 - saturated distilled water.

(c) Shake on a wrist action shaker for 24 hr.

(d) Let stand one hr.

(e) Filter through 0.45 μm filter.

(f) Analyze filtrate

This test was a physically severe method of assessing behavior of products should their structure break down with time in the disposal environment.

The slow shake test was used to assess the longer term behavior of intact specimens in contact with water. Products were molded by all vendors into cylinders 7.5 cm in diameter and approximately 20 cm long. Shake test steps are briefly described:

(a) Cut a cylindrical slice of approximately 100 grams from the fixed product (usually about 2 cm thick).

(b) Support the sample so that all sides are exposed to water in a glass jar. Add CO_2 - saturated distilled water in the ratio 10 mℓ H_2O:gram sample. Raw waste tests involved 50 gm sample and 1ℓ water.

(c) Oscillate jar at 60 one-inch strokes per hour.

(d) Sample and replace water every 48 hours. Analyze sample for components of interest.

Arsenic analyses were performed on a Perkin-Elmer Model 372 atomic absorption spectrophotometer. Digestions were conducted in a mixture of hydrofluoric, hydrochloric, and nitric acid within a tightly sealed Teflon vessel.

RESULTS

The leaching data for arsenic are presented for each waste type separately. Plots of concentration in the slow shake test leachate versus time, although not directly indicative of field conditions, allow some important inferences to be drawn. For example, if arsenic concentration for a sample were to continue at a high and stable level, leaching is probably limited by solubility. If the concentration drops with time, the available arsenic in the sample may be becoming depleted.

Figure 1 shows the slow shake test leachate arsenic data as a function of time. Both the raw waste and product C155 leached high arsenic concentrations early in the test, followed by a rapid decrease to low levels. In the case of the raw waste, all the arsenic in the sample dissolved. Here one can see the value of some fixation processes: for products A170 and F150, leaching has begun and continued at a much slower rate than in the raw waste. To compare this situation to rainfall and percolation events at a land disposal site, note that one such event would cause a large and sudden release of arsenic from unfixed wastes, while many such events would cause smaller and slower releases from a properly fixed waste.

(Fig. 1)

Elutriate test data for Waste No. 1 are shown in Table 1. (Samples from Process A could not be crushed into granular form.) Only Process F achieved any success in this destructive test.

(Table 1)

Leachate arsenic concentrations from slow shake tests for Waste No. 2 products are shown in Figure 2. Note that the early peak for the raw waste is much lower than that for Waste No. 1 because the solubility of As_2S_3 is lower than that of the organic arsenicals. The amount of arsenic leached from raw Waste No. 2 in the first ten days (five leachant renewal cycles) was only 25% of that initially present. The advantages of the fixation processes can be seen in that the initial leachate from the raw waste contained 40 mg/ℓ arsenic, while the leachate from the fixed wastes never exceeded 2 mg/ℓ.

(Fig. 2)

Table 2 lists elutriate test data for Waste No. 2. (Table 2)

It is interesting to note that the samples yielding high pH values in the elutriate were most successful in retaining arsenic. This behavior is unexpected because As_2S_3 is more soluble at high pH than at low pH. The more likely reason for this behavior is that these samples produced a large amount of clay-sized particles upon crushing, and that these particles adsorbed arsenic from the elutriate.

Data from slow shake tests on Waste No. 3 products are shown in Figure 3. In this case, the very soluble arsenic from the raw waste was found in the leachate early, and in continuing high amounts. Saturation of the samples' interstitial water probably prevents depletion of the available arsenic. A clear distinction among processes can be seen in Figure 3, with three orders of magnitude separating Processes B and F. (Processes C and D were similar in results to Process B).

(Fig. 3)

The elutriate data for Waste No. 3 do not show similar trends, as Table 3 illustrates. (Table 3)

One of the processes that was least successful in the slow shake test (Process D) performed very well in the elutriate test. The agitation that induces intimate

TABLE 1

ELUTRIATE TEST RESULTS
WASTE NO. 1

SAMPLE NO.	pH	SO_4(mg/l)	Cl(mg/l)	Mg As	% As LEACHED
B118	12.6	4,320	9,640	186	100
C155	7.1	8,750	24,800	880	100
D146	12.6	4,650	19,400	438	100
F150	5.5	9,630	16,700	120	27
RAW WASTE	5.7			540	100

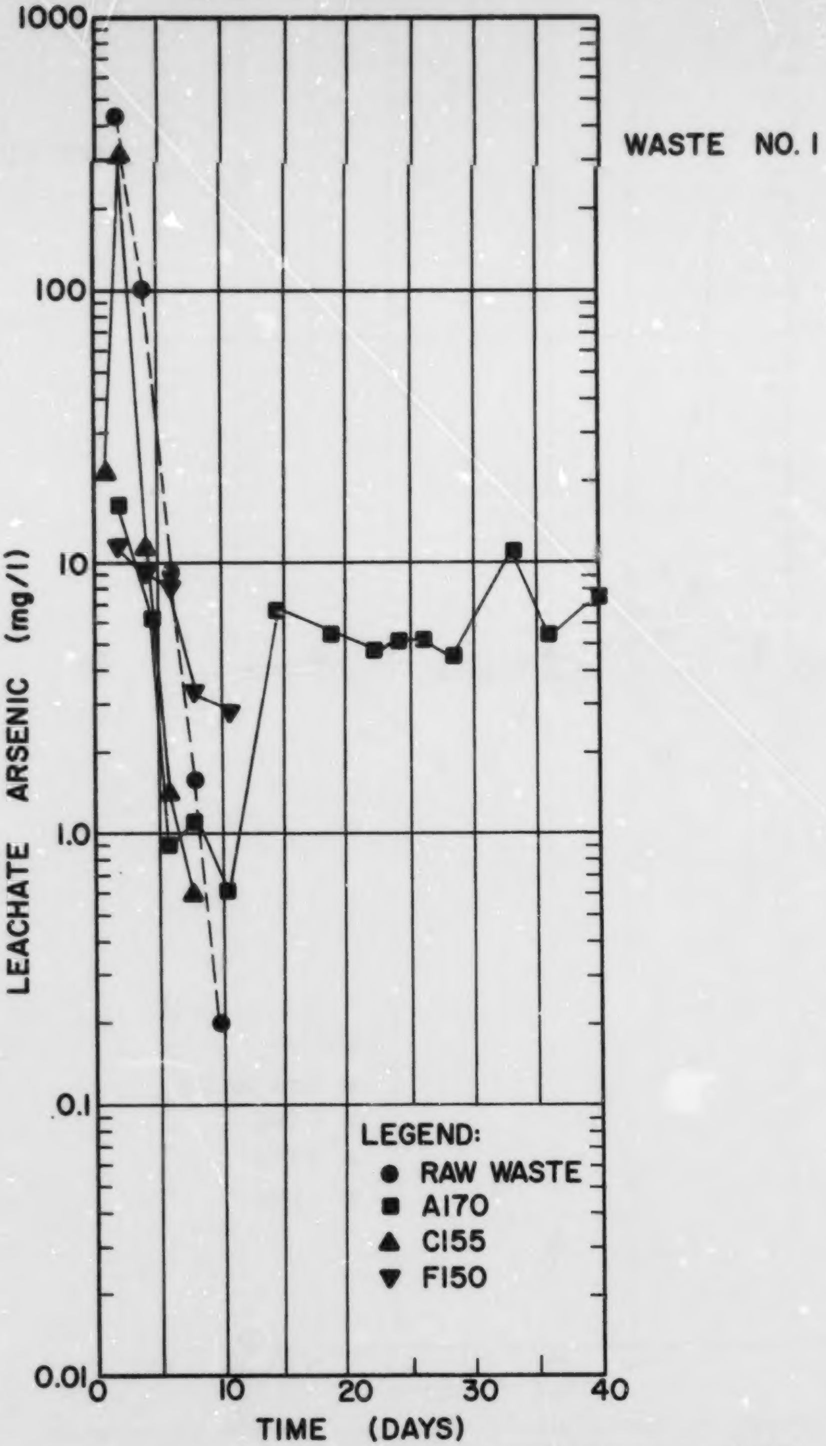

Figure 1. Effect of Time on Arsenic Concentration in Leachates: Slow Shake Tests, Waste No. 1

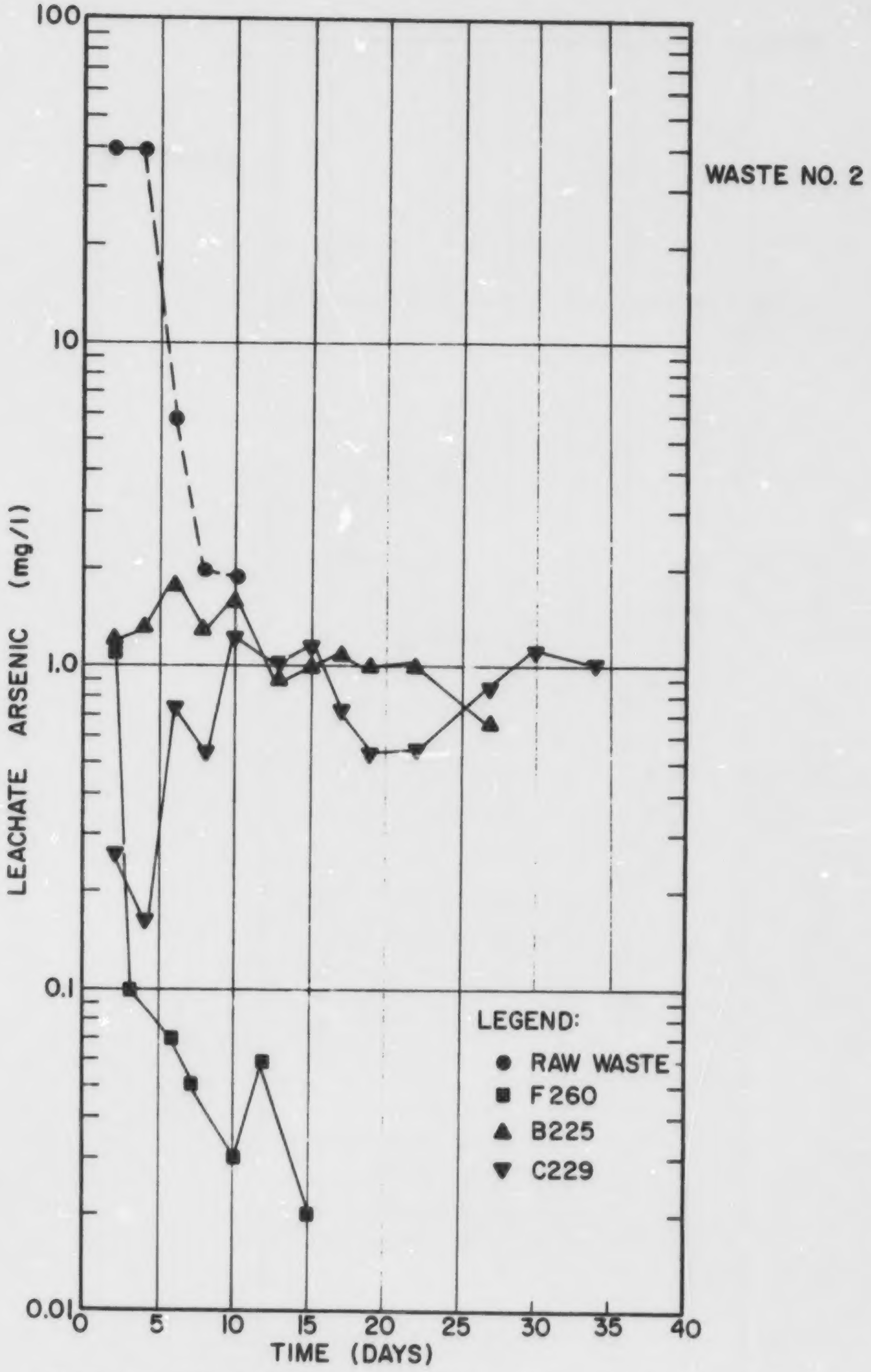

Figure 2. Effect of Time on Arsenic Concentration in Leachates: Slow Shake Tests, Waste No. 2

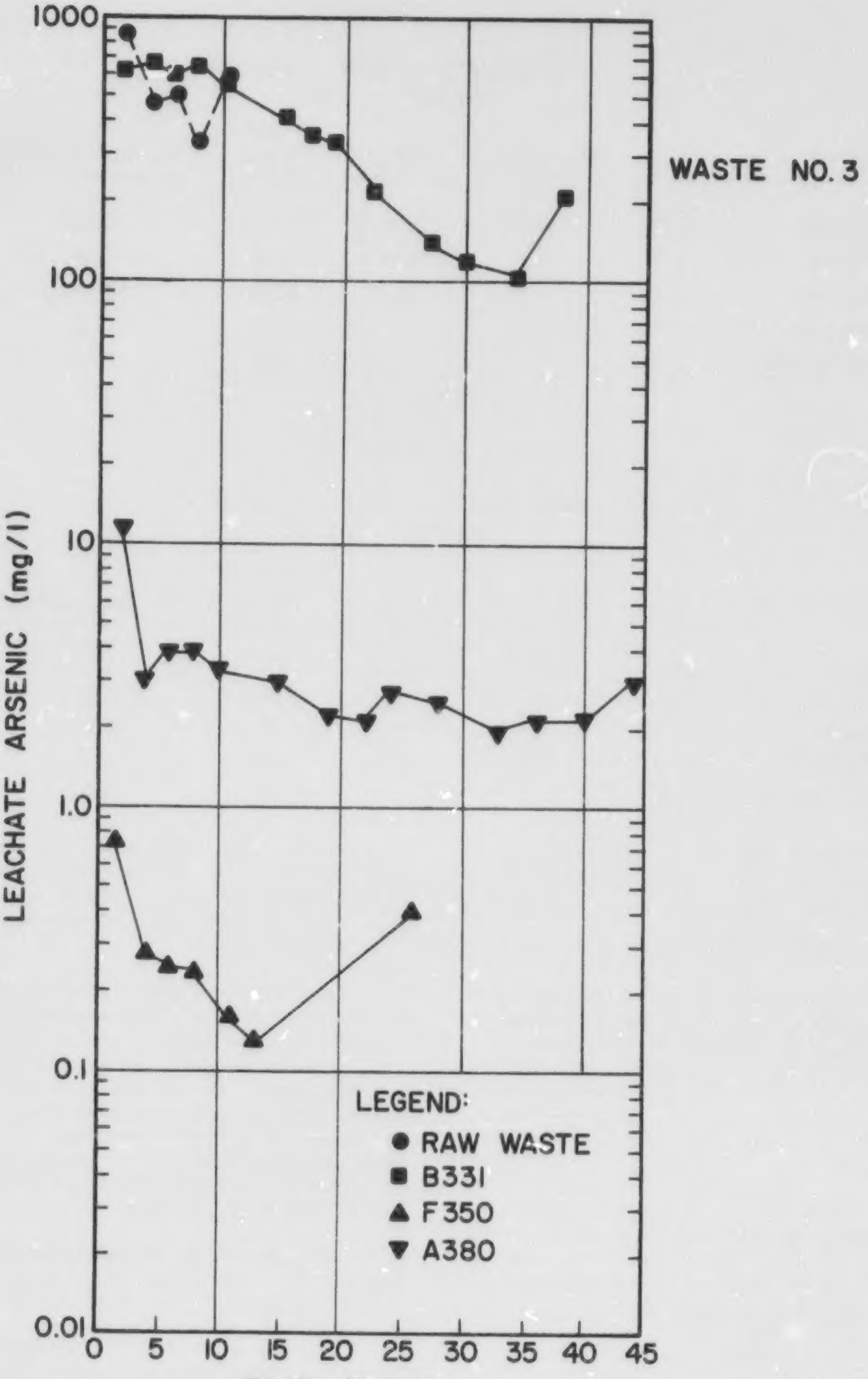

Figure 3. Effect of Time on Arsenic Concentration in Leachates: Slow Shake Tests, Waste No. 3

TABLE 2

ELUTRIATE TEST RESULTS
WASTE NO. 2

SAMPLE NO.	pH	SO_4(mg/l)	Cl(mg/l)	MgAs	% As LEACHED
B225	12.4	<0.2	22	0.04	0.02
C229	1.7	3.1	4.4	5.8	2.9
D228	12.5	1.5	22	<0.01	<0.005
F260	1.5	1,350		14	3.3
RAW WASTE	1.8			91	26

TABLE 3

ELUTRIATE TEST RESULTS
WASTE NO. 3

SAMPLE NO.	pH	SO_4(mg/l)	Cl (mg/l)	Mg As	% As LEACHED
B331	10.6	143	760	363	1.7
C370	2.4	1,050	3,060	3,160	6.6
D315	12.5	0.5	560	1.1	0.01
F350	4.3	550	1,650	80	0.2
RAW WASTE	3.2			9,100	27

contact between the small particles and the solution may promote an adsorption effect in this test.

DISCUSSION OF RESULTS

Further comparison and discussion of the two types of leaching tests follows, in an attempt to provide a rationale for future use of the tests and to develop criteria for evaluating the fixation processes. Tables 4, 5, and 6 compare the elutriate and shake test arsenic data for each waste.

(Table 4)

For Waste No. 1, Process F appears advantageous by both leaching tests. Other processes are less consistent; for example, Process B fared well in the shake test, but not in the elutriate test.

(Table 5)

As Table 5 shows, the data yielded by the two tests did not concur.

(Table 6)

Inconsistent trends are also observed in Table 6. The elutriate test suggests very good success for Process D, but shake testing does not prove this expectation. Process F, however, performed consistently well in both tests.

The elutriate test is brief and simple to perform, and it would therefore be desirable to show it as a useful predictive tool for the longer term leaching tests. Unfortunately, it appears that the elutriate test is not a consistent indicator of long-term arsenic leaching. It does have separate value as an indicator of leaching after a monolithic structure has broken down, however.

Interpretation of immersion tests such as the slow shake tests requires attention to the mass of pollutant leached. Data reported in studies on other industrial wastes (2) and on radioactive wastes (3,4) have used this approach. One useful way to view the data is to consider the mass of pollutant leached in relation to

TABLE 4

COMPARISON OF ELUTRIATE AND SHAKE TEST RESULTS
WASTE NO. 1

SAMPLE NO.	ELUTRIATE % As RELEASED	SHAKE CUMULATIVE % As RELEASED	
		1 DAY	8 DAYS
B118	100	1.4	14.5
C155	100	2.6	42.6
D146	100	25.8	38.2
F150	27	1.8	6.1
A170		1	3.9

TABLE 5

COMPARISON OF ELUTRIATE AND SHAKE TEST RESULTS
WASTE NO. 2

SAMPLE NO.	ELUTRIATE % As RELEASED	SHAKE CUMULATIVE % As RELEASED	
		1 DAY	8 DAYS
B225	0.02	0.25	3.2
C229	2.9	0.05	0.82
D228	<0.005	1.8	3.4
F260	3.3	0.12	0.31

TABLE 6

COMPARISON OF ELUTRIATE AND SHAKE TEST RESULTS
WASTE NO. 3

SAMPLE NO.	ELUTRIATE % As RELEASED	SHAKE CUMULATIVE % As RELEASED	
		1 DAY	8 DAYS
B331	1.7	0.89	15.4
C370	6.6	0.01	1.1
D315	0.01	2.0	6.7
F350	0.2	0.002	0.004

that initially available, and to accumulate the fractional mass leached in each leaching period. It is also helpful for those who would compare these data with other data from differently configured specimens to normalize the fractional mass with the volume: surface ratio. A plot, therefore, of the parameter

$$\frac{\Sigma a_n}{A_o} \cdot \frac{V}{S}$$

where: Σa_n = cumulative mass of arsenic leached in n periods
A_o = mass of arsenic initially present in sample
V = sample volume
S = sample apparent surface area

vs. time is shown in Figure 4 for Waste No. 1. Of the processes shown, Process C shows a very rapid increase in arsenic leaching, followed by a very slow rate of release. (A similar fixation process, performed by another vendor whose products are not discussed in this paper, showed almost identical behavior). This process almost immediately released all the arsenic in the product. The other processes shown in Figure 4 behaved more in accordance with similar plots reported in the literature (3,4).

(Fig. 4)

Figure 5 is a similar plot for Waste No. 2. Clearer differences among processes can be seen, especially from the low leaching rate of Process F. Performance of all processes shows significant improvement over the raw waste.

(Fig. 5)

Cumulative releases from products of Waste No. 3 are shown in Figure 6. The retention of arsenic by Process F in this case is three orders of magnitude better than the raw waste and Process D.

(Fig. 6)

The value of plots such as Figures 4 through 6 is to present a conceptually easy view of the relative success of the various processes. To gain a more rigorous quantitative figure of merit, it has been shown by Godbee and Joy (4), that a plot of the cumulative fraction leached versus the square root of time can be used. From such a plot, one can take the slope and calculate an effective diffusion coefficient for each product with the relation

$$\frac{\Sigma a_n}{A_o} \cdot \frac{V}{S} = 2\left(\frac{De}{\pi}\right)^{1/2} t^{1/2}$$

where: De = effective Diffusivity
t = time
and other symbols have been defined above.

Data are shown this way in Figures 7, 8, and 9 for Wastes 1, 2, and 3 respectively. The effective diffusion coefficients calculated from these plots are listed in Table 7.

(Table 7)

The approach to plotting the above equation should yield a straight line with slope equal to $2\left(\frac{De}{\pi}\right)^{1/2}$ if the underlying assumptions are valid. The primary assumption is that diffusion of arsenic to the surface of the solid is the limiting factor in leaching. For Wastes 2 and 3, the plots on rectangular paper are linear (the curves on Figures 8 and 9 appear nonlinear because semi-log paper was used to present the full range of leaching behavior). Thus evidence for a diffusion mechanism is present. For Waste No. 1 (Fig. 7) the plots of all products on both linear and semi-log paper are erratic. Therefore De values were not computed for Waste No. 1 products. The fractional amount of arsenic leached from Waste No. 1 products was consistently higher than for the other wastes in both types of leaching tests.

These observations suggest that Waste No. 1 requires treatment other than the processes discussed here to reach a diffusion-limited condition.

The slow shake tests discussed herein are continuing, so that endurance data on the products can be produced. In addition, other products remain to be subjected to leaching tests. The following conclusions, therefore, are tentative although they are well supported by the data presented here.

CONCLUSIONS

(1) Commercially available processes vary widely in their success in retarding leaching of arsenic from the wastes under study.

(2) For Wastes 2 and 3, all processes appeared to produce diffusion-limited leaching behavior.

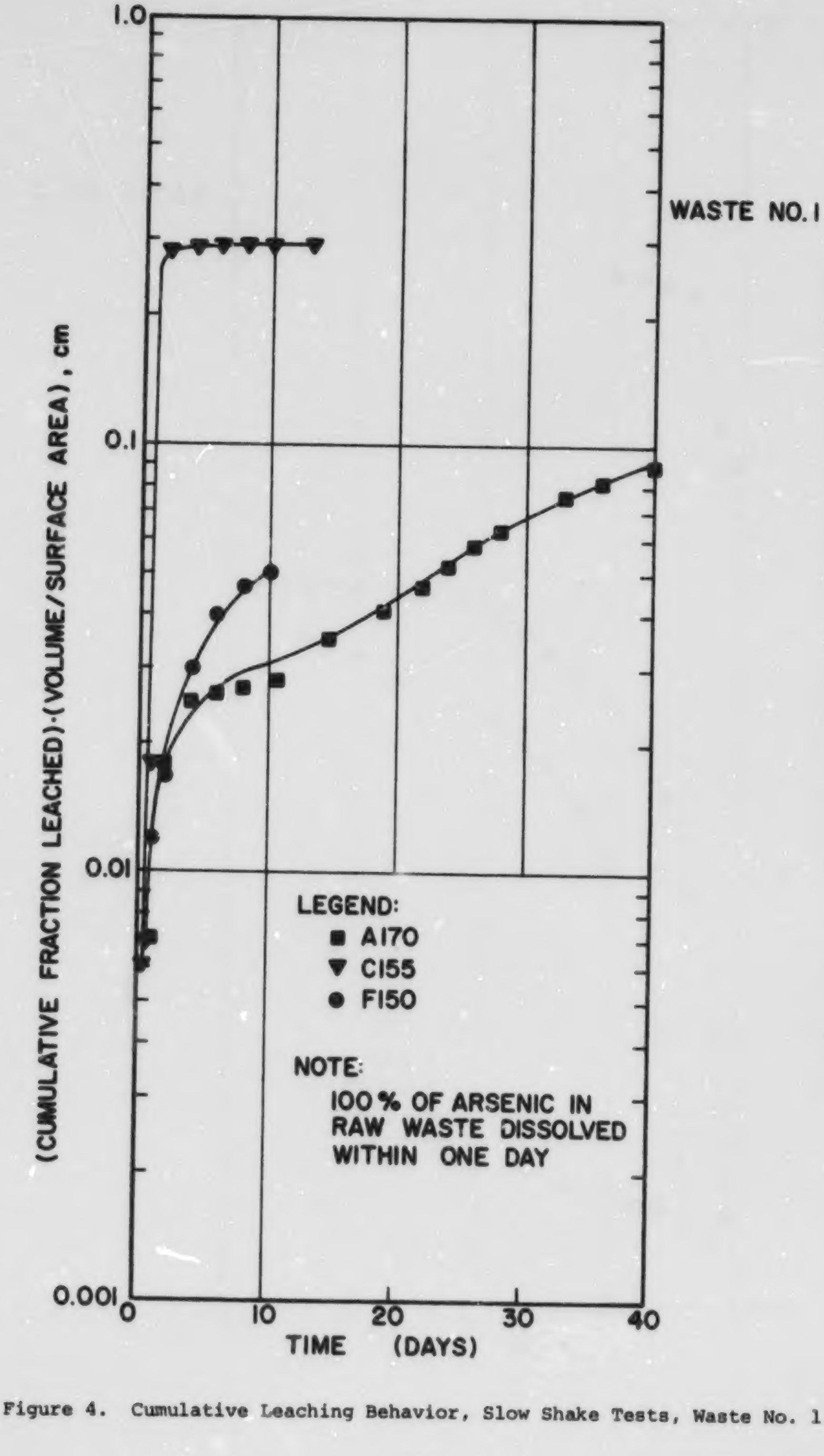

Figure 4. Cumulative Leaching Behavior, Slow Shake Tests, Waste No. 1

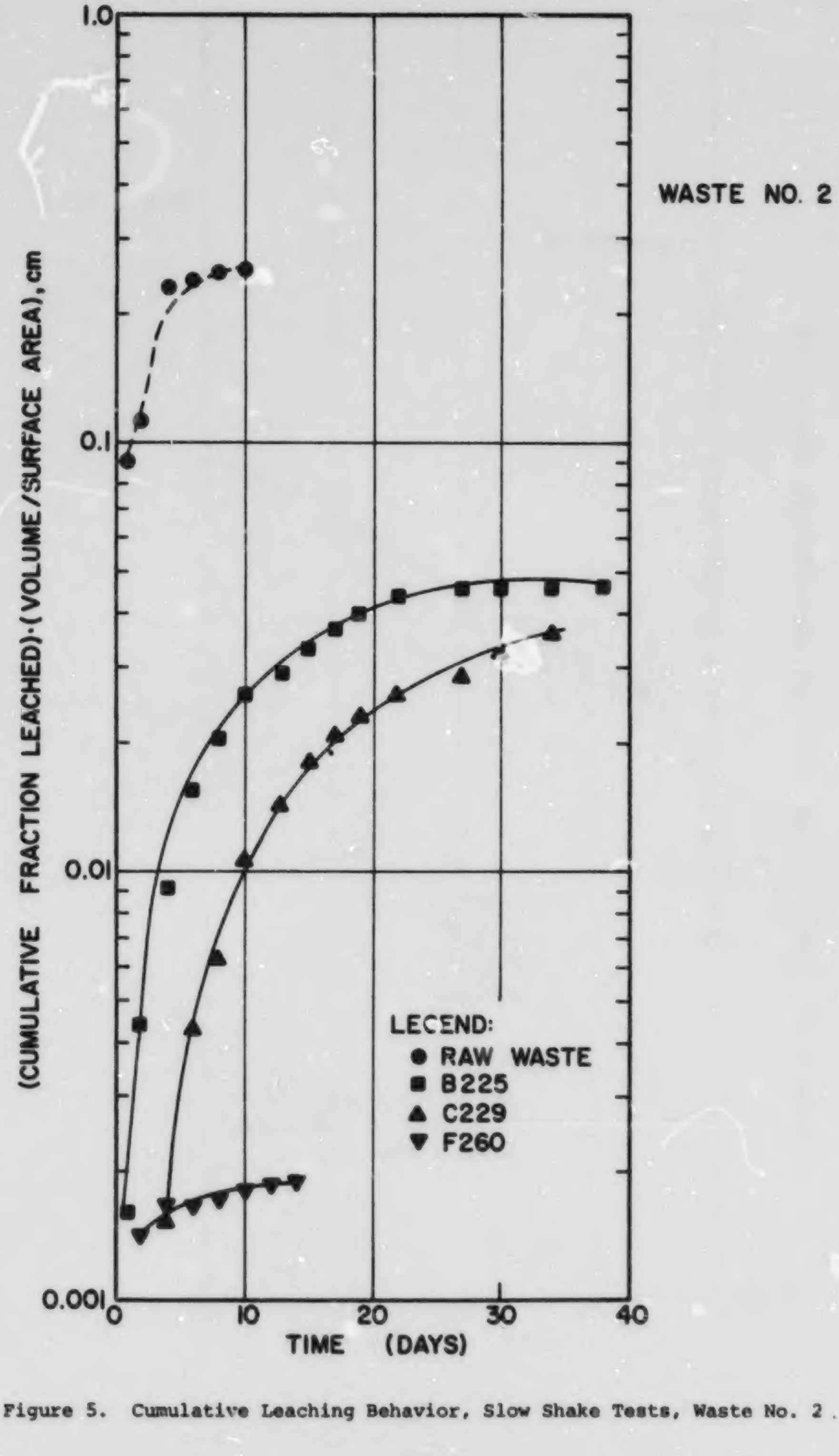

Figure 5. Cumulative Leaching Behavior, Slow Shake Tests, Waste No. 2.

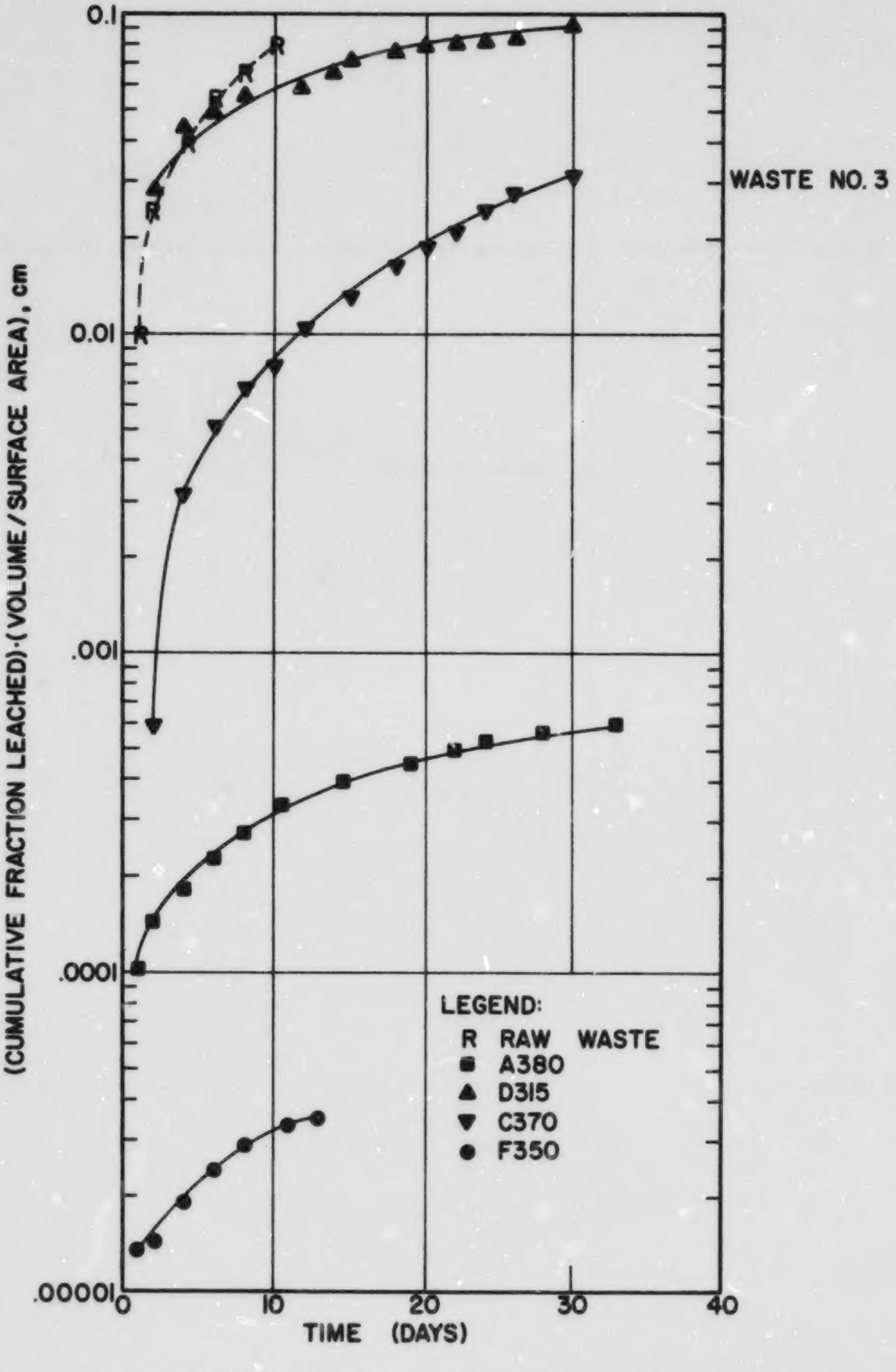

Figure 6. Cumulative Leaching Behavior, Slow Shake Tests, Waste No. 3

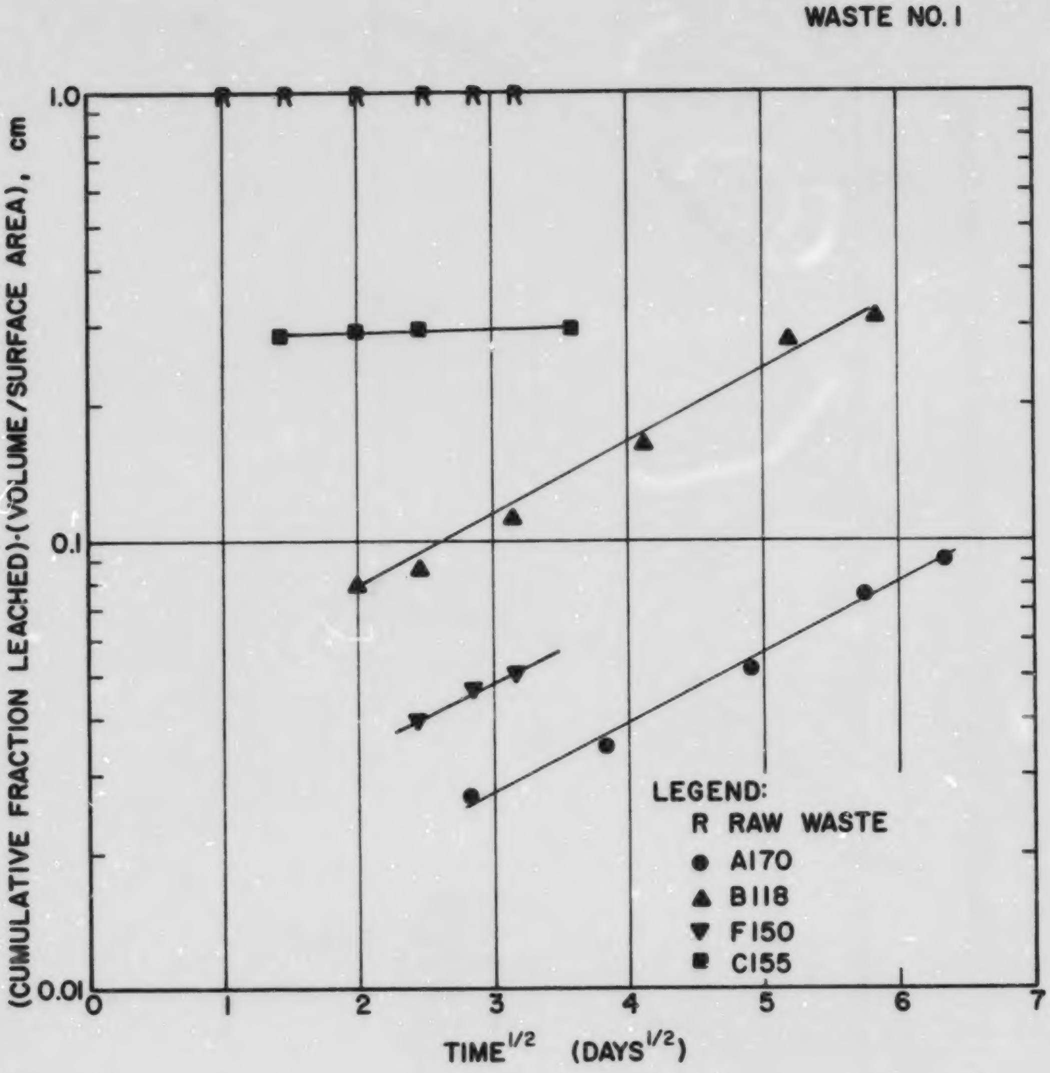

Figure 7. Diffusion Plot, Waste No. 1

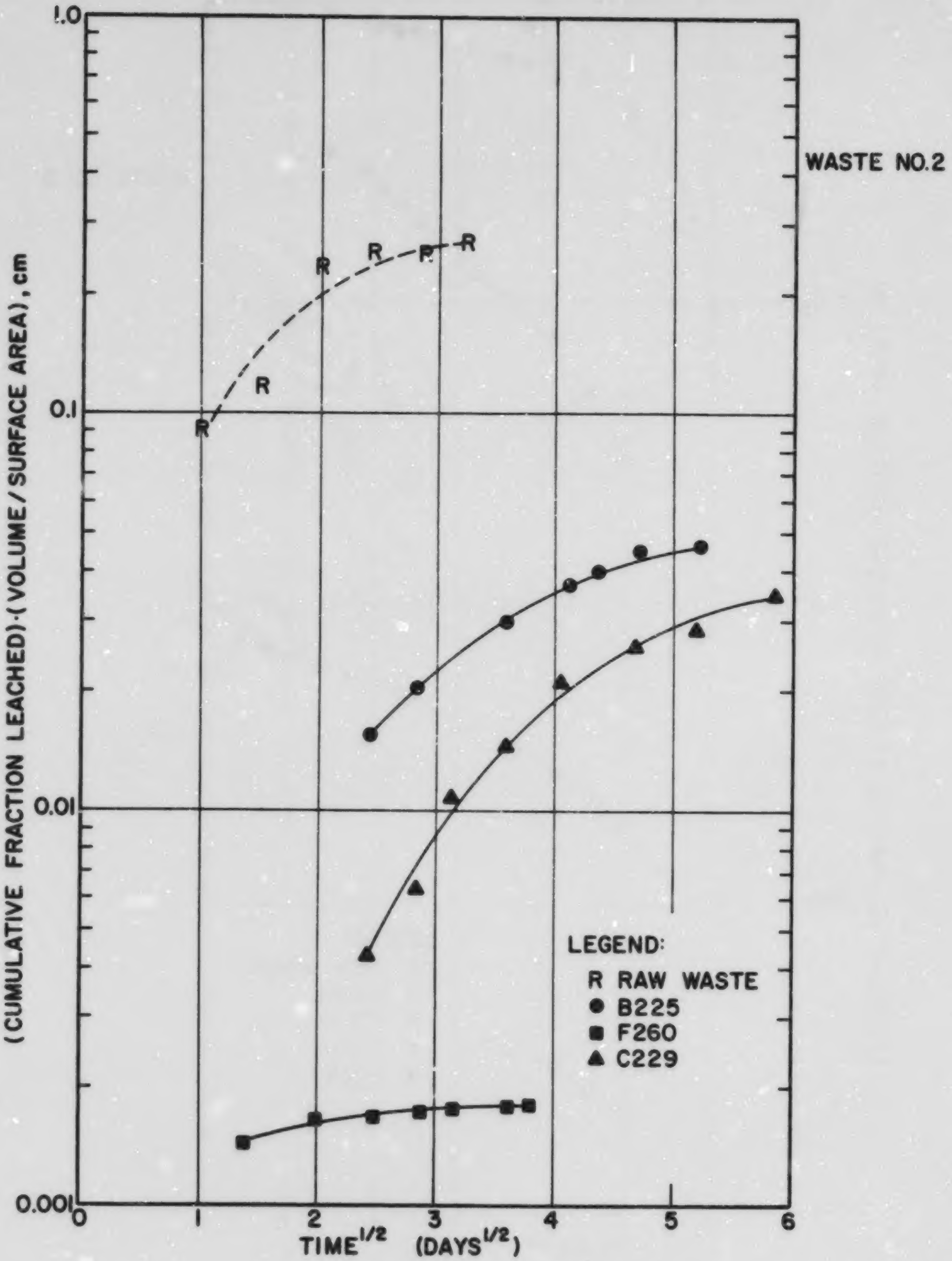

Figure 8. Diffusion Plot, Waste No. 2

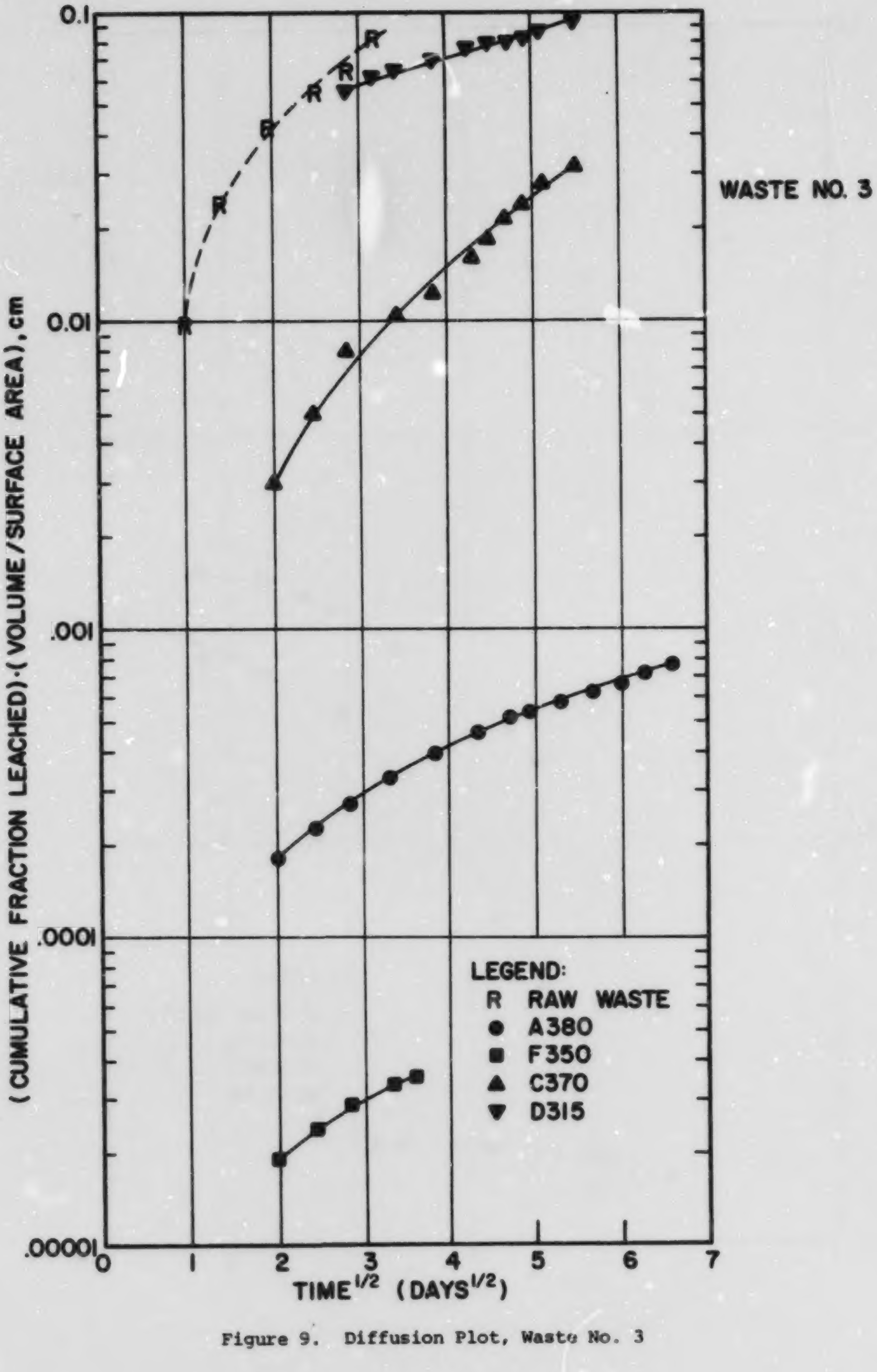

Figure 9. Diffusion Plot, Waste No. 3

TABLE 7

EFFECTIVE DIFFUSIVITIES OF FIXATION PRODUCTS

PROCESS	De (cm^2/day) WASTE NO. 2	 WASTE NO. 3
A		1.2×10^{-8}
B	9.6×10^{-5}	1.4×10^{-3}
C	6.9×10^{-5}	7.5×10^{-4}
D		1.7×10^{-4}
F	3.0×10^{-8}	4.1×10^{-10}

(3) For all three wastes, the elutriate test on crushed samples is not a reliable substitute for, or aid in predicting, long-term leaching behavior on monolithic specimens. It does yield useful information on the separate question of leaching behavior in the event that the monolithic structure should break down.

(4) The three wastes examined were quite different in their response to fixation attempts, as measured by leaching behavior. Waste No. 1 produced the least success with all processes discussed here.

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ENCAPSULATION TECHNIQUE FOR CONTROL OF HAZARDOUS MATERIALS

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ABSTRACT

A process using polyolefins and fiberglass to encapsulate containers holding hazardous wastes was researched, developed and evaluated on a laboratory scale. The process is geared to reinforce deteriorating containers in order to secure their hazardous consignments in subsequent handling operations and under environmental conditions existing in a direct disposal site such as a landfill. Polyolefins were employed because they provide a unique combination of low cost, abundance, chemical stability, mechanical toughness and flexibility. Fiberglass is low cost, prevalent, chemically stable, stiff and load bearing. Encapsulate test specimens (right cylinders, 3-inch dia. x 4-inch ht.) were fabricated by fashioning cylindrically shaped fiberglass casings, having walls about 1/50-inch thick, and then forming 1/4-inch thick jackets by fusion of powdered high density polyethylene (HDPE) upon the surfaces of the casings. The test specimens were thus rendered seamless. Mainly, two types of specimens were produced, some filled with sand and some hollow. A set of sand-filled ones were charged with aqueous solutions of heavy metals (simulating loss of container contents within an encapsulate) and then examined with respect to their ability to secure metal contaminants under aqueous leaching conditions. They were found to hold their contents secure in leaching by water and by a strong solvent for metals such as dilute hydrochloric acid. Hollow and filler containing specimens were employed to evaluate mecahnical performance of encapsulates. These, under appreciable mechanical pressure, were found to maintain their dimensional integrity. Under extreme pressures, they underwent distortion, yet their jackets did not fail even though their casings were flawed by the mechanical stresses. The above results indicate the processes' ability to prevent, or limit to acceptable levels, the release or delocalization of hazardous waste from deteriorating containers in manipulation and in final disposition. This paper discusses the process and provides results of the evaluations. Since the process is viewed as a constituent aspect of a general approach being developed for encapsulation of hazardous materials, the encapsulation technique applied in earlier work for managing unconfined, particulated, hazardous wastes is reviewed.

INTRODUCTION

Encapsulation technique being developed at TRW under EPA sponsorship is addressed to management of wastes which are potentially harmful to man and/or the environment, and in addition, difficult to control by current means.[1,2] For many hazardous wastes current waste management schemes are found wanting. Either contaminants, inherently, cannot be "neutralized", e.g., heavy metals, or they are difficult to render harmless, as in incineration of highly haloginated organic compounds. When heavy metals are "stabilized" by chemical fixation, a pretreatment step may be required. Yet the fixed metal contaminants may exhibit stability under ambient conditions that are more benign than those they may encounter in environments designated for final waste disposition. Furthermore, pretreatment in many cases must be tailored to the contaminant type thereby making complex mixtures difficult to manage. Under the above circumstances, encapsulation becomes an attractive alternative technique for hazardous waste management.

In the management of difficult to control wastes by encapsulation, a singularly important feature must be general applicability. It is recognized that means not applicable directly to essentially all the outstanding difficult to control wastes would be of limited utility. For example, it would be prohibitively expensive and complex to match waste types with technique designated appropriate. Nor is it acceptable to carry out pretreatment of wastes to render them chemically suitable for a particular approach. However, concentration of hazardous contents may be suitable so that more cost effective use can be made of encapsulating materials and product manipulation procedures.

The waste types under study are:

- Particulates (Unconfined Wastes)
- Containers (Preconfined Wastes)
- Sludges (Unconfined Wastes)

Work was carried out initially with respect to encapsulation of particulated wastes.* The particulates employed were obtained by dewatering selected sludges The present study concerns encapsulation of containerized wastes, i.e., 55-drums and smaller containers holding hazardous consignments.** Although experimental work presently is not being carried out in management of sludges per se, one objective of the work is to fit sludges (without dewatering) into the encapsulation technique.

Description of previous study of particulated waste encapsulation is given here; and in addition, new aspects of this work are provided. Greater emphasis is given to description of the present study. In this respect, fabrication of laboratory scale test specimen encapsulates and evaluation of products, presently completed, are described in some detail. This work is scheduled for completion in August 1978.

NATURE OF WASTE ENCAPSULATES

TRW hazardous waste encapsulates are characterized by two essential elements: a stiff, load bearing moiety, and a tough, flexible, seamless plastic jacket. The stiff element is geared to provide dimensional stability under mechanical stresses an encapsulate may encounter in manipulation, transportation and final disposition such as a landfill. Jacket secures the hazardous consignment in the event the encapsulate encounters inordinate mechanical stresses causing dimensional distortion that may give rise to flaws in the load bearing element. And furthermore, the jacket plays the important role of sealing the encapsulate and securing the contaminants vis-a-vis environmental leaching waters.

The selection of materials and encapsulate fabrication technique are interdependent. But the jacketing materials were fixed because it was deemed desirable to employ polyolefins as jackets for encapsulates because polyolefins are mass produced, low cost, well characterized and exhibit excellent chemical compatibility and mechanical performance. On a price/performance these materials are unique. Thus the objectives of encapsulation studies were to establish ready method for jacket formation using polyolefins, and therewith to determine concomitant means for encapsulate fabrication.

Encapsulation of Particulated Wastes

Encapsulations of waste particulates were carried out on a laboratory scale by cementation of particulates with an organic binder, thus fashioning load bearing agglomerates, and then enveloping the agglomerates with jackets of polyolefinic plastic. Test specimens were produced in two shapes; cubic, 3-inches on edge and cylindrical, 3-inch dia. x 4-inch ht. The resin 1,2-polybutadiene was selected for fashioning agglomerates. This resin was shown to exhibit the unique feature of readily consolidating particulates having a wide range of chemical compositions and consistencies. Consolidation occurred under minimal mechanical pressures by chemical reaction in the presence of waste concentrations up to 97% by weight yielding agglomerates with densities over 100 lbs per cu ft. The agglomerates were then secured by 1/4-inch thick **jackets** of high density polyethylene (HDPE). (A commercial scale encapsulate, e.g., a cubic shape two feet on edge, is expected to weigh about 800 to 1000 pounds and require about 8% by weight total resin for its fabrication.) The jackets were formed by fusing powdered HDPE upon the surfaces of the agglomerates. This method of jacket formation was selected and developed because it required only minimal mechanical pressures and no molten resin displacements, thereby simplifying jacket formation. Jackets were thus rendered seamless.

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*Contract Nos. 68-03-0089 and 68-03-2037, Solid and Hazardous Waste Research Division, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268

**Contract No. 68-03-2483

The encapsulates were found to exhibit excellent chemical stability and mechanical performance. With chemical reaction in agglomerate formation, 1,2-polybutadiene yielded binders chemically cross-linked having backbones characterized by singly bonded carbon atoms, chemical configurations that exhibit exceptionally high resistance to hydrolytic and oxidative degradation and yield stiff substances. The agglomerates were indeed found to be chemically stable and high load bearing. The HDPE jackets sealed the agglomerates and thus secured the hazardous contents with respect to delocalization by aggressive aqueous solutions. The encapsulates withstood appreciable mechanical pressure until finally yielding their dimensional integrity, yet with dimensional distortion their hazardous consignments remained secure due to the tough, seamless plastic jackets.

Continuing exploratory work was oriented to making agglomerates exhibit more "plastic" than ceramic yield modes under extreme mechanical pressures. The incorporation of powdered polyethylene into the agglomerate indicated that plastic character can be imparted in this manner. There were also excellent indications that polyethylene was grafted chemically onto the polybutadiene structure in agglomerate formation, thereby polyethylene when molten remained homogeneously dispersed in the agglomerates.

This phenomenum gave rise to the concept that agglomerate formation can be carried out with simultaneous plastic encapsulation of the particulates thus negating the need for jacket formation. However, this apparent advantage may be counter-balanced in realizing high performance contaminant containment by the need to specify suitable particulate consistencies, a need practically eliminated when jacket formation is employed. With respect to jacket formation, the exploratory work oriented to demonstrate that polyolefins other than HDPE may be readily utilized. Thus evidence was garnered that ultra high molecular weight polyethylene and chemically cross-linkable polyethylene were indeed utilizable. Future investigation should demonstrate utilization of polyethylene ionomers and polybutadiene treated polyethylenes. The above polymer types, in our opinion, could lead to two or three jacket formulations wherewith essentially the overwhelming portion of hazardous waste may be securely encapsulated.

Encapsulation of Containerized Wastes

In management of containerized wastes by encapsulation, it was assumed that the walls of containers would eventially corrode, and subsequently containers would not be load bearing. As a result, mechanical stresses would be transferred to the encapsulate walls. In contrast to particulated waste encapsulates wherein jackets need not be load bearing, containerized waste jackets need to provide load bearing character.

Fiberglass was selected as the stiff element to reinforce polyethylene jackets because this material exhibits a unique combination of features: low cost, prevalence, chemical stability and mechanical stiffness. Methods for its use utilize well developed state-of-the-art techniques. Spray-up is the preferred method; however, in the laboratory the convenient method of hand lay-up was employed.

Fiberglass reinforced polyethylene encapsulate test specimens were produced in the laboratory cylindrically shaped, 3-inch dia. x 4-inch ht., with walls of two-layer construction. The walls consisted of about 1/4-inch thick polyethylene jackets backed by 1/50-inch thick fiberglass. (The thickness and nature of the fiberglass moiety in a commercial scale encapsulate would be characterized in future work to withstand mechanical stresses an encapsulate may encounter in real-life manipulation and final disposition. A commercial scale encapsulate is envisioned to provide about

75 gallons capacity. The wall would consist of a 1/4-inch thick polyolefin jacket backed by a 1/16 to 1/8-inch thick chopped fiberglass casing. The jacket and the casing would comprise by percent of the encapsulate volume about 3.5 and 1.8, respectively.) The purpose of the laboratory test specimens was to provide demonstration of high chemical and mechanical performance for fiberglass reinforced polyethylene encapsulates.

Some encapsulates were produced containing sand, some containing plastic microballons, and some hollow. The sand filled ones were charged with aqueous solution of heavy metals (simulating loss of container contents within an encapsulate) and then examined with respect to their ability to secure metal contaminants under aqueous leaching conditions. (Sand or soil would be used to fill voids between containers and container/encapsulate walls. Compaction of containerized wastes rather than filler utilization was considered to be potentially desirable because it gives rise to more effective use of encapsulating materials and product manipulation methods. But compaction operations may also require pollution control procedures which may be burdensome, hazardous and costly. As a result, encapsulation technique was initially tailored to manage hazardous waste containers as is.) Hollow ones and some sand and microballon ones were employed to evaluate the mechanical performance of encapsulates. It was assumed that a clearer picture of encapsulate wall performance would be realized by more detailed examination of encapsulates without filler than those with filler.

ENCAPSULATION TECHNIQUE AND ENCAPSULATION EVALUATIONS

The following sections show (a) laboratory procedure for preparing encapsulation test specimens, (b) performance of specimens in leaching by aqueous solutions, and (c) performance under extreme mechanical stresses. Further evaluations of the test specimens are underway with completion of studies scheduled in August 1978. The initial results indicate that polyolefin/fiberglass encapsulation of wastes should yield commercial scale, high performance products. Although cost studies are yet to be completed, it is our opinion that on a cost/performance basis polyolefin/fiberglass encapsulation would provide an attractive alternative for control of hazardous materials existing in containers.

Fabrication of Polyethylene Encapsulate Test Specimens

Figure 1 shows construction sand being poured into the glass/resin casing (cocoon), and the following figure (Figure 2) shows the encased sand product.

Fusion of polyethylene was carried out in the annulus resulting from positioning an encased product in a mold as shown in Figure 3. Polyethylene was then placed as shown in Figure 4. And the polyethylene was fused as in Figure 5.

The steel mold walls were heated by hot mold plattens, with the rise in temperature of the mold walls monitored by a thermal probe. The changes in phase of the polyethylene, i.e., powdered resin to molten resin, and then subsequently to solidified resin with cooling of the mold walls, was readily observed on the pressure gauge. The speed of jacket formation was essentially limited only by the heat exchange rate. (Commercially, 1/4-inch thick polyethylene products are fabricated in 30 seconds.)

The specimen stemming from the operation in Figure 5 is shown in Figure 6; Figure 7 shows the injection of a solution of hazardous chemical agents into the cavity. (The solution occupies the space between the sand particles.)

Employing additional polyethylene powder, the encapsulation of the test specimen was completed, as shown in Figure 8. (In multiple specimens the following metals were localized: Ni, Cd, Hg, Cr, Zn, Cu, Sb, As, Se, and Pb. The specimens were placed in plastic containers holding 1500cc of leaching solution. Plastic in contrast to glass allows ready agitating and tumbling of the ensembles.) Figure 9 shows container holding specimen in leaching solution.

A specimen residing in the container is shown in Figure 10. The set of test specimens in leaching is shown in Figure 11.

Preliminary Leaching Results

Table 1 contains preliminary analytical determinations of the heavy metal containing encapsulates immersed in deionized water. Table 2 pertains to metals immersed in 0.1N HCl leaching solution.

Initial analytical determinations were performed on a Jarrell-Ash Atomic Absorption

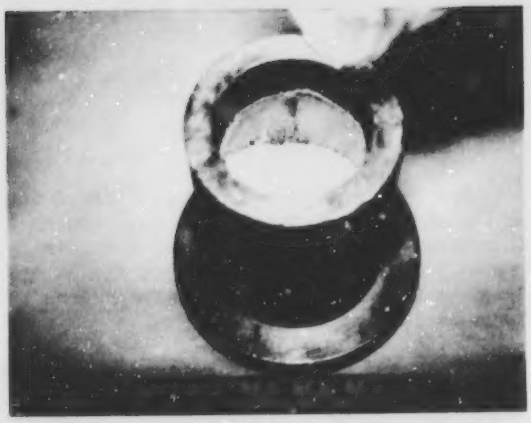

FIGURE 1. SHOWS FABRICATION STEP OF GLASS/RESIN ENCASEMENT OF SAND

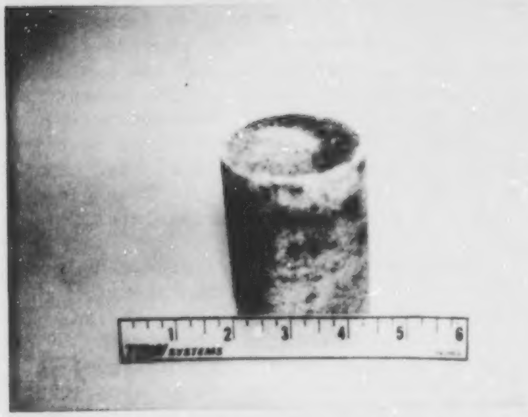

FIGURE 2. CLASS/RESIN ENCASED PRODUCT

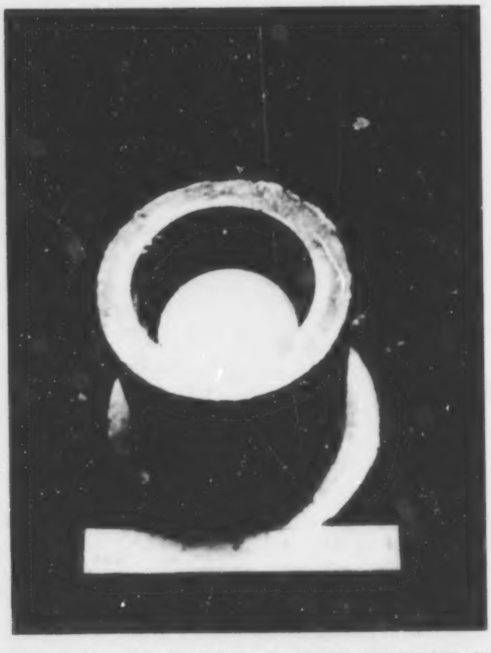

FIGURE 3. AN ENCASED PRODUCT CENTERED IN MOLD FOR POLYETHYLENE ENCAPSULATION

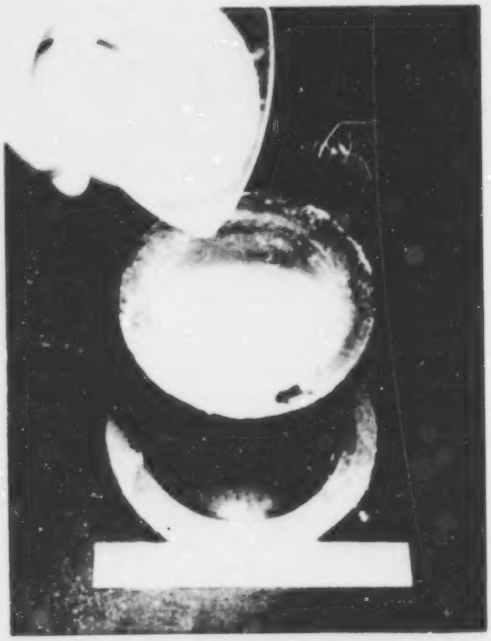

FIGURE 4. SUBMERGING ENCASED PRODUCT WITH POWDERED POLYETHYLENE

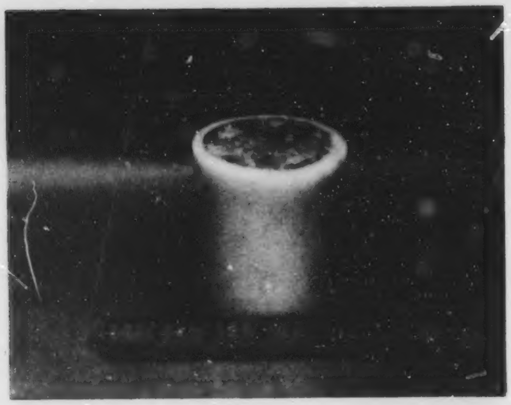

FIGURE 6. A POLYETHYLENE ENCASED PRODUCT STEMMING FROM THE FIRST FUSION STEP

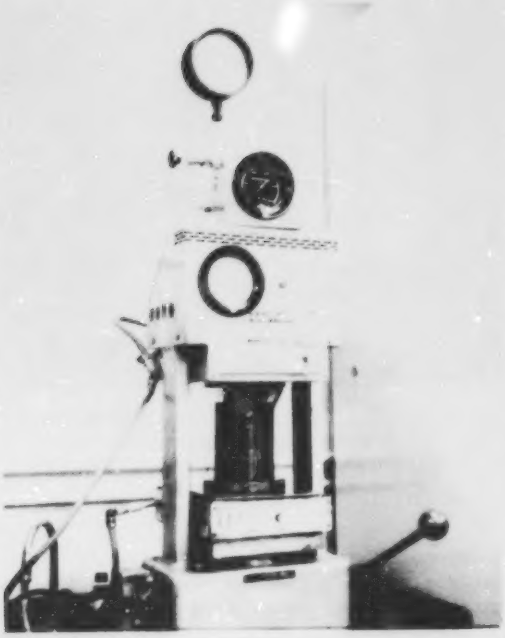

FIGURE 5. APPARATUS EMPLOYED FOR FUSING POWDERED POLYOLEFIN

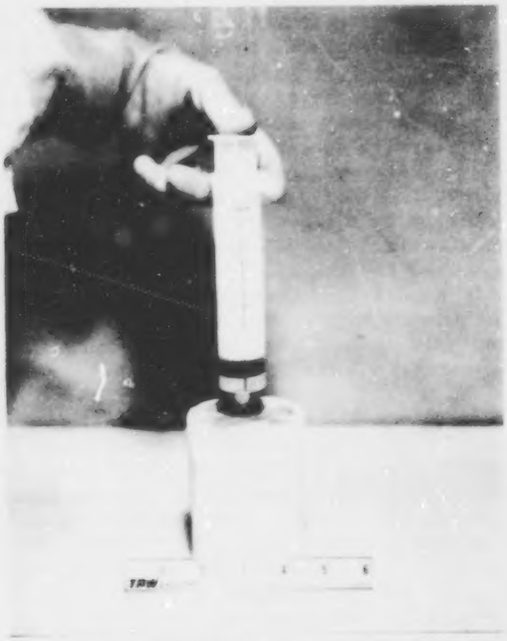

FIGURE 7. HAZARDOUS CHEMICAL AGENTS BEING INJECTED INTO THE TEST SPECIMEN

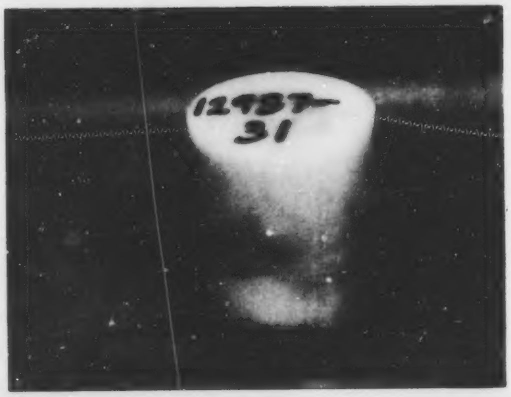

FIGURE 8. COMPLETED POLYETHYLENE ENCAPSULATED TEST SPECIMEN

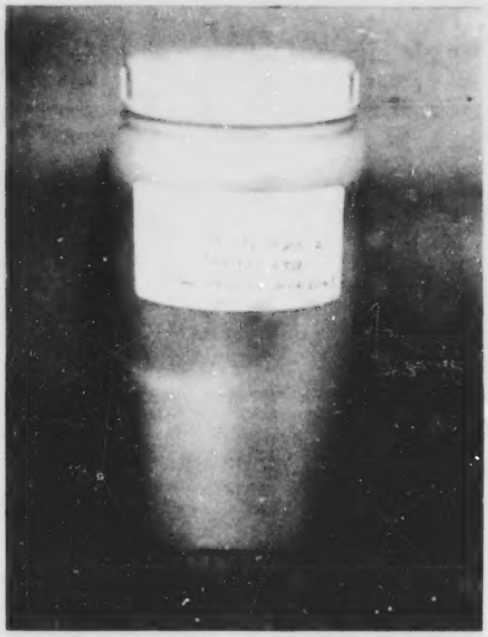

FIGURE 9. SHOWS CONTAINER TYPE FOR HOLDING SPECIMEN IN LEACHING SOLUTION

FIGURE 10. SHOWS SPECIMEN RESIDING IN CONTAINER HOLDING LEACHING SOLUTION

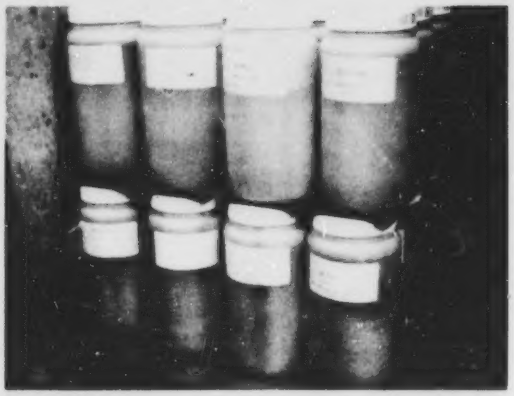

FIGURE 11. SHOWS SET OF SPECIMENS IN LEACHING SOLUTIONS

Spectrophotometer, model 850. Detailed analyses are now underway employing instrumentation and techniques with lower detection limits.

Compressive Specimens and Properties

The response mode of cylindrical polyethylene encapsulate specimens were investigated to increasing mechanical loads applied to specimens in vertical and lateral positions. (Figures 12, 13, 14, 15 and 16 show the response of a vertical encapsulate to progressively increasing compressive stress.) All specimens were compressed to 40% of their original vertical heights. The specimens recovered about 90% of their heights with release of the applied compressive loads. Hollow encapsulates exhibited two bulges, as shown in Figure 17, while sand filled ones, showed single bulges as shown in Figure 18. No explanation is presently on hand that accounts from these two observed modes of deformation.

Figures 19 and 20 show the response modes of encapsulate under lateral compression. Under extreme degree of compression about 75%, no rupture of the encapsulate was observed. With release of tne applied load, the specimen recovered to about 70% of its lateral dimension. The nature of the encapsulates resulting from lateral compression are shown in Figures 21 and 22. (The "circles" on the compressed encapsulates stemmed from the imprints on the faces of the compressive rods.)

TABLE 1. METAL CONCENTRATIONS (PPM) IN DEIONIZED WATER LEACHING SOLUTION*

Metal	Day** 90	Day 120	Metal Loss*** (Calculated)	Comments
As	-	0.002 (±0.001)	1000	
Cd	<0.05	0.0006 (±0.0006)	800	These encapsulated waste concentration values are within the variation of the background "instrumental noise".
Cr	<0.05	0.007 (±0.0005)	810	" " "
Cu	<0.05	0.009 (±0.001)	3190	" " "
Hg	< 2	0.005 (±0.0003)	820	" " "
Ni	<0.5	0.007 (±0.003)	810	" " "
Pb	<1.0	0.003 (±0.002)	1000	" " "
Sb	<1.0	0.040 (±0.002)	860	" " "
Zn	<0.05	0.003 (±0.003)	2070	" " "
Se	-	0.117 (±0.011)	860	-

*Change in sensitivity of values reflects employment of more definitive analytical techniques

**"Day" - Number of days encapsulated waste immersed in deionized water

***"Metal Loss" - Values calculated giving concentrations of contaminates in leaching solutions assuming catastrophic failure of specimens.

TABLE 2. METAL CONCENTRATION (PPM) IN 0.1N HCl LEACHING SOLUTION*

Metal	Day** 60	Day 90	Metal Loss*** (Calculated)	Comments
Ni	<0.5	0.010 (±0.003)	810	These encapsulated waste concentration values are within the variation of the background "instrumental noise".
Sb	<1.0	0.040 (±0.002)	860	" " "
Zn	<0.05	0.006 (±0.003)	2070	" " "

*Change in sensitivity values reflects employment of more definitive analytical techniques

**"Day" - Number of days encapsulated waste immersed in HCl leaching solution

***"Metal Loss" - Values calculated giving concentrations of contaminates in leaching solutions assuming catastrophic failure of specimens.

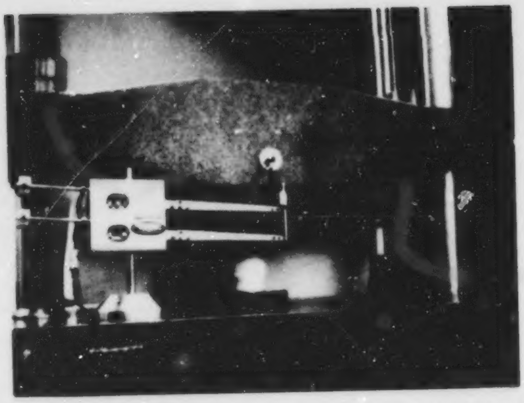

FIGURE 12. ONSET OF BULGING OF ENCAPSULATE UNDER COMPRESSION STRESS

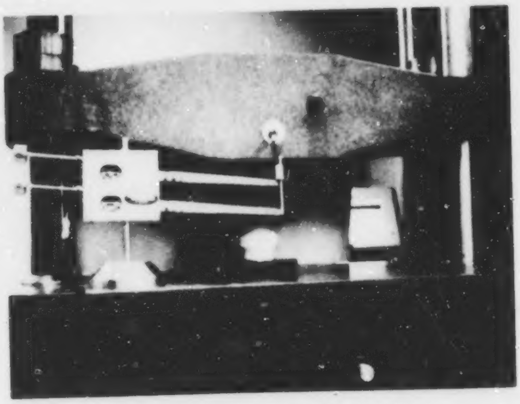

FIGURE 13. BULGING PRONOUNCED AT SPECIMEN MIDDLE

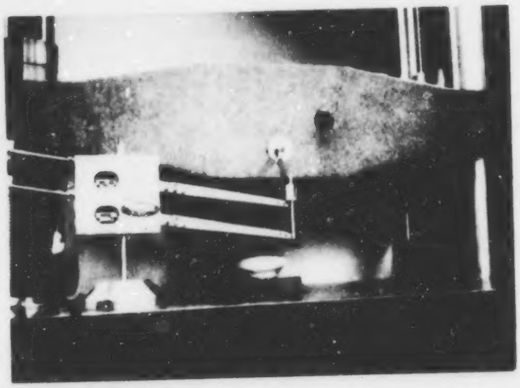

FIGURE 14. FURTHER BULGING

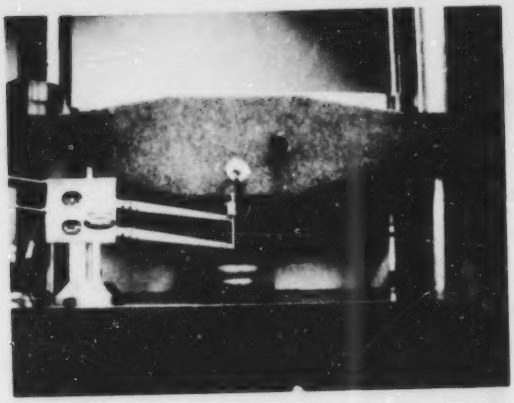

FIGURE 15. "VASE" LIKE CONFIGURATION

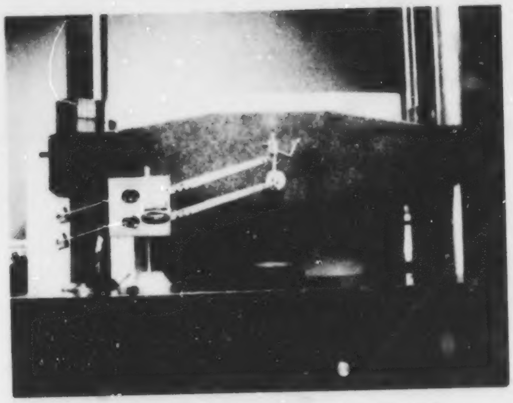

FIGURE 16. ENCAPSULATE UNDER EXTREME COMPRESSION

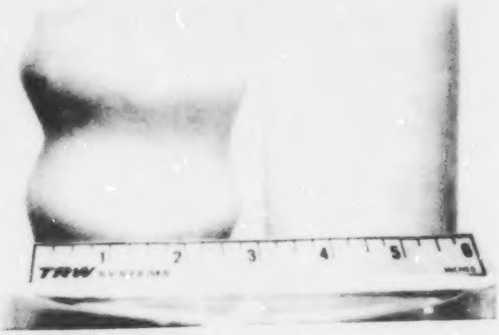

FIGURE 17. SHAPE OF HOLLOW ENCAPSULATE RESULTING FROM COMPRESSION

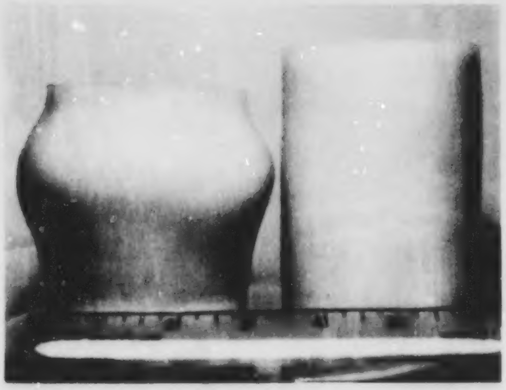

FIGURE 18. SHAPE OF FILLED ENCAPSULATE RESULTING FROM COMPRESSION

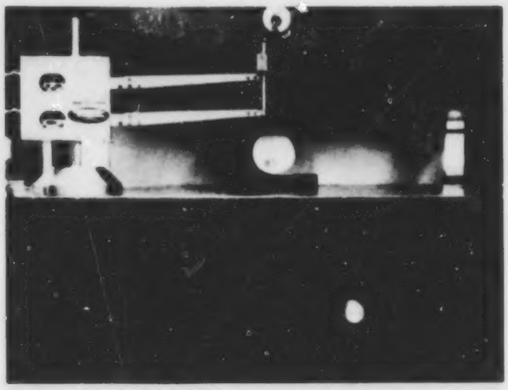

FIGURE 19. ENCAPSULATE POSITIONED FOR LATERAL COMPRESSION

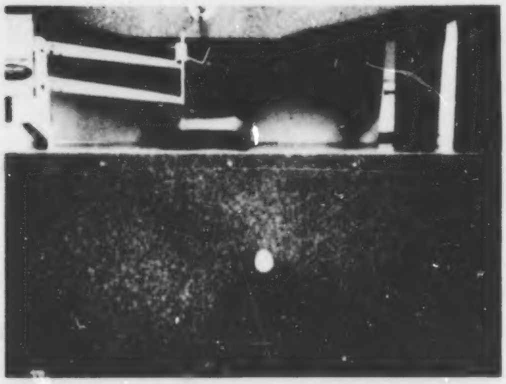

FIGURE 20. SIDE VIEW OF ENCAPSULATE IN LATERAL COMPRESSION

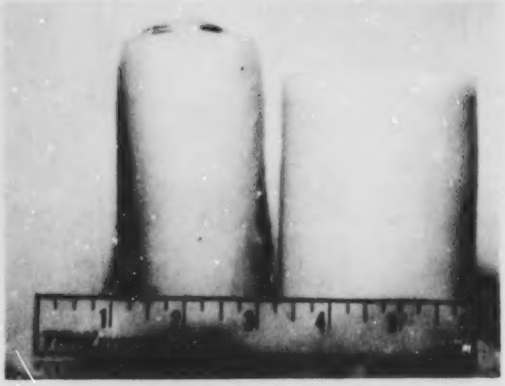

FIGURE 21. SIDE VIEW OF ENCAPSULATE AFTER LATERAL COMPRESSION

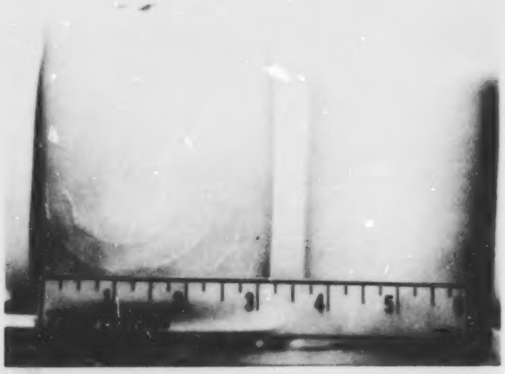

FIGURE 22. FRONT VIEW OF ENCAPSULATE AFTER LATERAL COMPRESSION

The ability of the encapsulates of this work to undergo extreme lateral compression without failure is a feature of these structures that is, in our opinion, not characteristic of conventional containers. (Conventional containers fitted with lids will not undergo appreciable lateral compression without rupture of the lid-container wall interface. With respect to maintaining a water tight configuration, even minimal degrees of compression would be detrimental.

Figure 23 shows graphically the response of a hollow encapsulate under compressive load. The influence of the stiff casing is clearly noted on the graph by the spiked portion of the curve which is emphasized in Figure 24. This is characteristic of brittle materials such as glass fiber reinforced epoxy composites. In contrast to catastro-

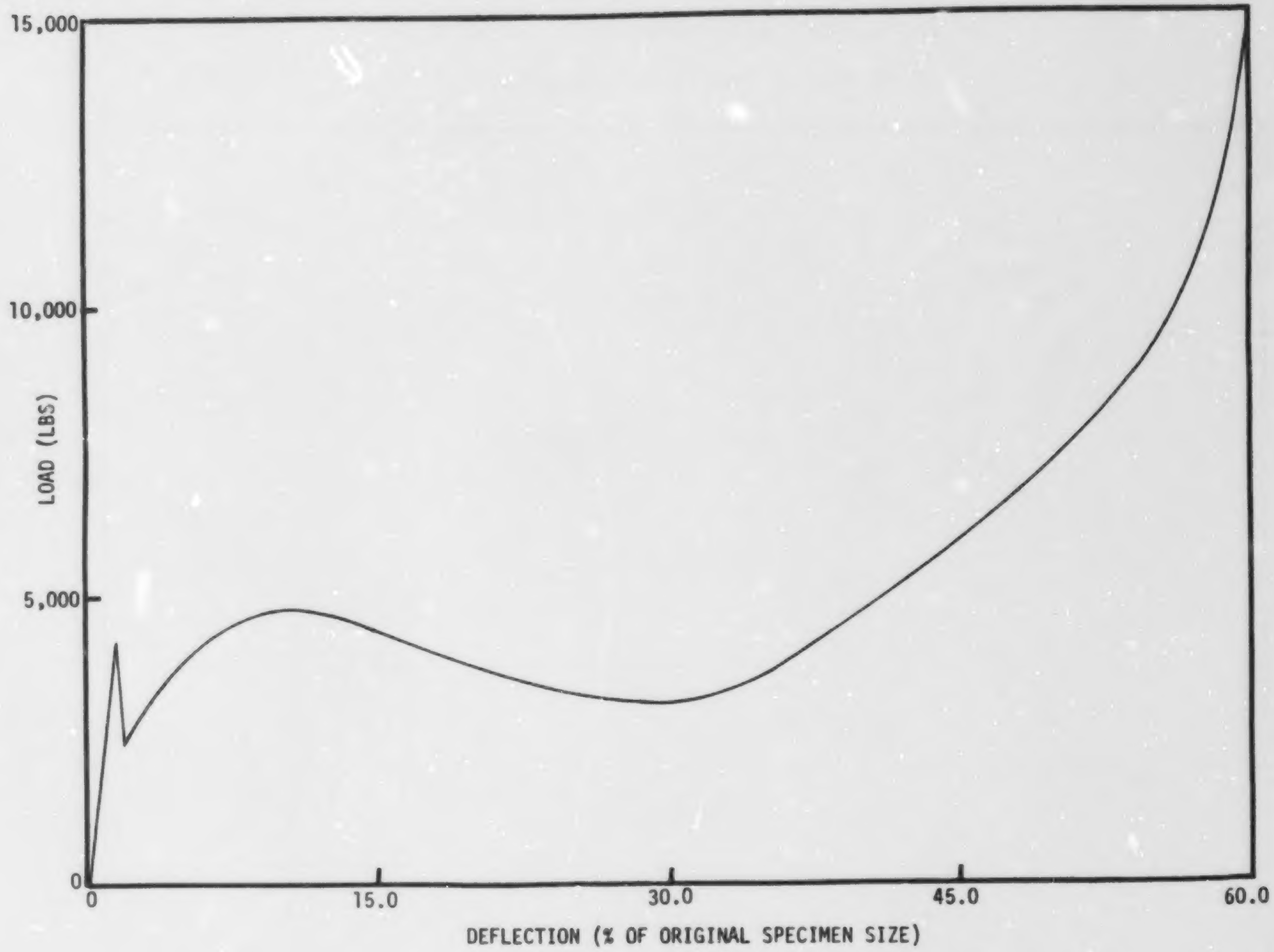

FIGURE 23. LOAD-DEFLECTION OF HOLLOW ENCAPSULATE

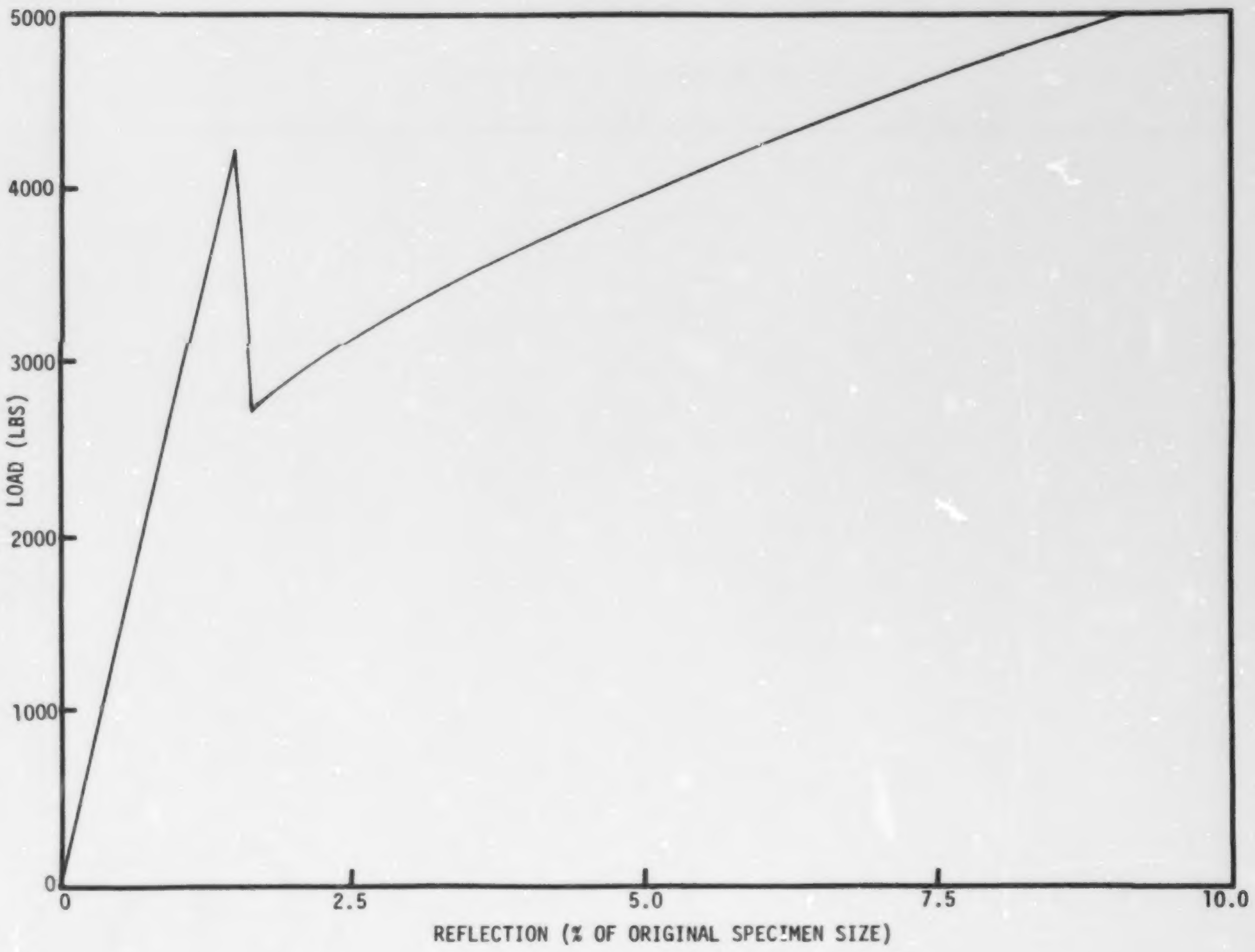

FIGURE 24. LOAD-DEFLECTION OF HOLLOW ENCAPSULATE

phic property loss of such materials, the encapsulates continue to exhibit load bearing properties due to presence of the jacket. The remaining portion of the curve reflects the influence of the jacket. Up to 30% deflection the curve is characteristic of polyethylene in tension. This is most likely due to the jacket being subject to tensile stresses as the casing undergoes flawing compression. After 30% compression, the apparent load bearing properties of the hollow encapsulate increases dramatically. This may be due to continuing flawing of the casing while the encapsulate is being compressed thereby introducing more plastic jacket as load bearing material.

A view of the cross-section of a hollow encapsulate after compression to about 40% of its original vertical height is given in Figure 25. One notices the high degree of fragmentation of the casing. The fragments stemmed mainly from the vertical inner walls while the casing remained essentially intact on top and bottom of the cavity. Almost all the vertical casing was sheared from the jacket upon extreme compression of the encapsulate. The jacket, however, did not fail.

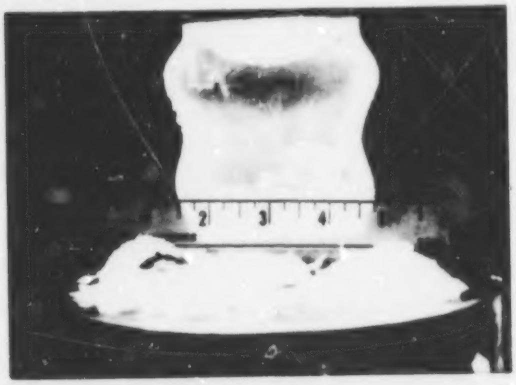

FIGURE 25. SHOWS FRAGMENTATION OF THE CASING AND FUNCTIONAL INTEGRITY OF THE JACKET AFTER GREAT EXTENT OF COMPRESSION

An inner view is given in Figure 26 of an encapsulate with sand filler which underwent extreme vertical compression. In this case the casing of the filled encapsulate was not fragmented to the degree seen for the hollow one. One notices, however, the casing to be appreciably crazed. Nevertheless, the jacket remained intact; there were no apparent breaks nor was there any apparent change in its cross-sectional dimension.

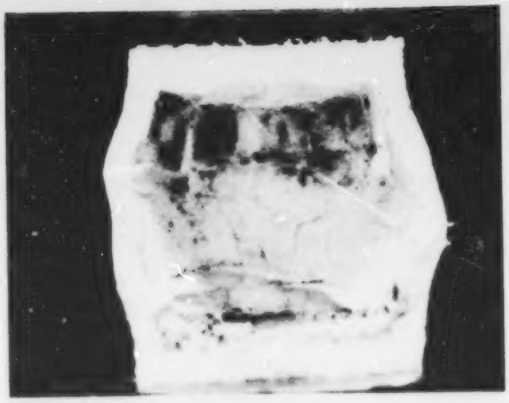

FIGURE 26. INNER VIEW OF ENCAPSULATE AFTER GREAT EXTENT OF VERTICAL COMPRESSION

An inner view is given in Figure 27 of an encapsulate that contained plastic hollow sphere filler (simulating containers) and underwent extreme extent of lateral compression. In these cases, appreciable fragmentation of the casing occurred at the vertical extremities, while the casing disposed laterally was relatively unaffected. One can see the crease in the casing traversing down the center caused by the great extent of lateral compression. In lateral compression, as well as in vertical compression, the jackets of the encapsulates were found to retain their functional integrity.

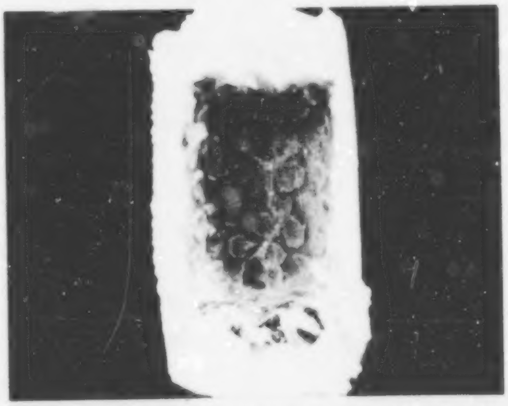

FIGURE 27. INNER VIEW OF ENCAPSULATE AFTER GREAT EXTENT OF LATERAL COMPRESSION

CONCLUSIONS

Results of the study and evaluations described in this paper led to the following conclusions:

- Polyethylene jackets backed by fiberglass casings yield encapsulates exhibiting excellent chemical and mechanical properties.
- Jackets are readily formed by fusion of powdered polyethylene onto the surfaces of casings.
- Thick jackets can be rapidly formed.
- Encapsulates of polyethylene and fiberglass can be fabricated in the presence of unconfined aqueous solutions in the cavities. Based upon the process evaluations, the process appears to be compatible with a wide range and condition of containerized hazardous wastes which may not be adequately manageable by other techniques.
- Based upon performance in laboratory tests, encapsulated containerized wastes would be expected to provide a high degree of control over the release to the environment of unwanted quantities of hazardous wastes tested.
- Based upon literature characterization of polyolefins, control of an extensive range of hazardous and corrosive materials would be expected.

DISCUSSION AND RECOMMENDATIONS

Studies are still in progress with respect to encapsulation of containerized wastes with polyolefins and fiberglass. The trend of the current work indicates that fusion of powdered polyolefins onto glass casings give rise to jackets having the expected properties of polyolefinic resins. Consequently, the extensive information supplied by the resin manufacturers for these plastics can be applied directly to estimating their performance as jackets of encapsulated wastes. An objective of future work should be selection of two or three polyolefinic resins which are compatible with the bulk of hazardous waste types and exhibit high performance chemical and mechanical properties. In this respect, HDPE is an excellent candidate material. In addition, the required nature and thickness of the fiberglass casings should be defined wherewith encapsulates may withstand real-life stresses.

Additional study is recommended to determine means to fabricate commercial scale encapsulates of containerized wastes, particularly 55-gallon drums, under actual field conditions. This study should give rise to an encapsulation unit that is readily transportable to the site where containerized wastes reside. At that site, encapsulation of containers should be carried out. The managed containers are thus made suitable for transportation to and sequestering in a direct disposal site.

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2. Lubowitz, H.R., Derham, R.L., Ryan, L.E. and Zakrzewski, G.A., "Development of a Polymeric Cementing and Encapsulating Process for Managing Hazardous Wastes", U.S. Environmental Protection Agency Report, EPA-600/2-77-045, August 1977.

FIELD EVALUATION OF CHEMICALLY STABILIZED SLUDGES

by

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Vicksburg, Mississippi 39180

ABSTRACT

Four sites where stabilized industrial wastes had been disposed were examined to determine the effects of stabilized wastes on surrounding soils and groundwater. All areas selected for study were in the humid eastern or southern United States where rainfall was sufficient to produce abundant leachate. The sludges had all been fixed using the same proprietory process involving addition of cementitious materials to form a stable, soil-like product. Two of the industrial waste sites contained auto assembly (metal finishing) wastes, one site contained electroplating wastes and the fourth site contained refinery sludges. The physical properties of soils under the disposal sites were affected little, if at all, by the disposal operation. At one of the auto assembly waste disposal sites, high background levels of constituents in the groundwater masked any escape of pollutants from the fixed sludge. Elevated levels of chloride, calcium and sodium were found in groundwater under and down the groundwater gradient from the disposal area at the second auto assembly plant. Only elevated levels of sulfate and boron were found under and down the groundwater gradient from the electroplating waste site. Elevated levels of sulfite, nitrite, cyanide, phenols, and arsenic were noted in groundwater under and down dip from the disposal area at the refinery site. Toxic metal contamination in groundwater was not a serious pollution problem at the sites studied at the time of the survey.

INTRODUCTION

A recent EPA-funded survey of 50 typical land disposal sites that received large volumes of industrial wastes showed that 43 of the dumps, landfills or disposal lagoons had caused some degradation of local groundwater quality (1). The most frequently occurring inorganic contaminants from industrial solid waste were selenium, barium, cyanide, copper, and nickel. Levels of hazardous inorganic substances that exceeded concentrations set in Federal drinking water standards were found at 26 sites. The most common pollutants found in excessive amounts were selenium, arsenic, chromium and lead.

Careless disposal of industrial solid wastes particularly electroplating sludges, refinery sludges or wastes containing paint has, in the past, caused severe degradation of groundwater quality. In Nassau County, New York, electroplating wastes leached chromium and cadmium into the local groundwater forcing surrounding water supply wells to be abandoned. Sludges containing paint wastes were buried in an abandoned sand and gravel pit in Maryland. Monitoring wells showed that the level of hexavalent chromium in local groundwater rose to 7.2 mg/liter; far above levels safe for human consumption (2). At Alma, Michigan, refinery wastes (containing phenols) were buried in a pit in a shallow, glacial aquifer. The resulting high phenol levels in groundwater caused the condemnation of two nearby water-supply wells (3).

The current investigation was under-

TABLE 1. SUMMARY OF CHARACTERISTICS OF THE FOUR SITES SELECTED

Characteristic	Site W	Site X	Site Y	Site Z
Geographic area within the U. S.	Central	North Central	North Central	South Central
General geologic setting	Glacial Drift	Glacial Outwash	Pleistocene - Lake Terrace	Deltaic - Fluvial Deposits
Mean annual rainfall	102 cm	93 cm	88 cm	117 cm
Mean annual air temperature	12°C	11°C	10°C	21°C
Nature of waste	Paint, putty	Electroplating	Paint, putty	Refinery sludge
Major pollutants detected in sludge analyses	B, Cr, Fe, Pb, Mn, Ni, Zn	Cd, Cr, Cu, Mn, Na, Zn	Cr, Fe, Pb, Mn, Zn	Pb, Mn, and phenol
Liner used below fill	None	None	None	None
Thickness of waste	1.22-3.05m (avg. 2.14m)	0.91-1.22m (avg. 1.07m)	Thin*	1.83-3.20m (avg. 3.79m)
Nature of material in unsaturated zone	Sandy clay	Sandy clay	Clayey sand	Clay
Thickness of unsaturated zone	3.05-8.60m (avg. 5.60m)	2.16-2.93m (avg. 2.41m)	1.46-11.80m (avg. 8.79m)	1.04-6.63m (avg. 3.79m)
Average hydraulic conductivity below waste	1.1×10^{-7} cm/sec	3.45×10^{-7} cm/sec	2.63×10^{-4} cm/sec	4.2×10^{-7} cm/sec
Character of covering material	None	None	None	Clay
Average thickness of cover	0.0	0.0	0.0	0.5m
Dates of emplacement of fixed sludge	1974	1973	1974*	1974
Type of operation	Diked fill	Diked fill	Fill	Diked fill and cover

* Fixed waste was placed on the ground in April and May 1974; but, the major portion of the fixed material was removed to a landfill in Jaunary 1975 when the area was regraded.

taken to determine if the stabilization or "fixation" of industrial sludges could be shown by field investigations to prevent the loss of contaminants into surrounding soil and groundwater. Four sites where stabilized industrial sludges containing electroplating, paint, or refinery wastes had been placed were examined. Borings were made to groundwater at each site and samples of soil and groundwater were collected for testing or chemical analysis. The principal physical characteristics of soil samples beneath and outside the disposal sites were examined. A randomization procedure was used to detect differences between experimental samples collected under the landfills and down the apparent groundwater gradient and control samples collected up the apparent groundwater gradient. The major features associated with the four industrial disposal sites studied are summarized in Table 1. Analyses of the fixed sludges placed at each site are given in Table 2.

MATERIALS AND METHODS

Sampling Procedures

At each site eight to ten borings were made to the water table using a truck-mounted drill rig equipped with a 16.8-cm diameter, hollow-stem auger The locations of borings at each site are given in Figures 1-4. Soil samples were obtained by removing the central plug from the auger and forcing an Hvorslev fixed-piston sampler or a split-spoon sampler into the soil or sediment. Care was taken

TABLE 2. CONCENTRATIONS OF MAJOR CHEMICAL CONTAMINANTS IN THE FIXED SLUDGE AT EACH SITE*

Constituent	Site W (mg/kg)**	Site X (mg/kg)	Site Y (mg/kg)	Site Z (mg/kg)
B	43	35	10	25
Cd	4.5	105	0.1	1.3
Cr	250	1600	30	36
Cu	28	1650	18	12
Fe	47,000	4000	23,500	8900
Pb	40	20	40	215
Mn	850	110	572	160
Ni	75	50	30	8
Se	1	1.3	0.42	0.5
Na	350	1281	2000	236
Zn	1300	650	200	45
Hg	0.05	0.20	0.02	0.3
Phenol				Present

** On a dry wt basis.

* Data obtained from companies involved and analyses of sludge samples.

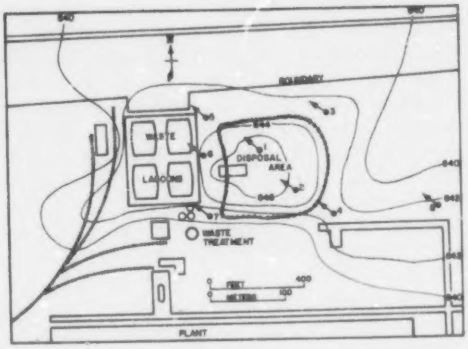
N
BOUNDARY
WASTE
LAGOONS
DISPOSAL AREA
WASTE TREATMENT
FEET
METERS
400
100
PLANT
644
646
640
642

FIGURE 1. LOCATION OF BORINGS AT SITE W ARROWS INDICATE MOST PROBABLE DIRECTION OF GROUND WATER MOVEMENT.

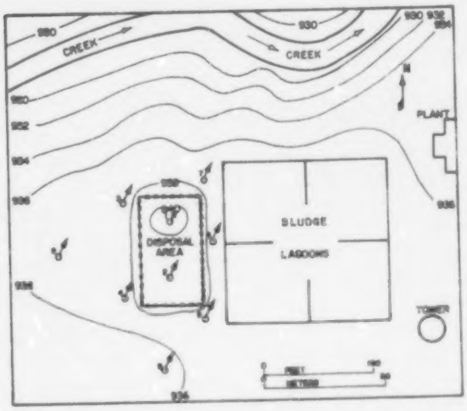
CREEK
CREEK
930
N
PLANT
SLUDGE
LAGOONS
DISPOSAL AREA
TOWER
FEET
METERS
936

FIGURE 2. LOCATION OF BORINGS AT SITE X ARROWS INDICATE MOST PROBABLE DIRECTION OF GROUND WATER MOVEMENT.

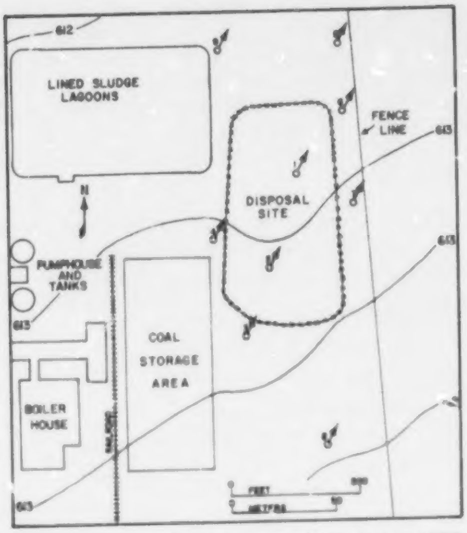
612
LINED SLUDGE LAGOONS
FENCE LINE
613
N
DISPOSAL SITE
PUMPHOUSE AND TANKS
COAL STORAGE AREA
BOILER HOUSE
RAILROAD
FEET
METERS

FIGURE 3. LOCATION OF BORINGS AT SITE Y ARROWS INDICATE MOST PROBABLE DIRECTION OF GROUND WATER MOVEMENT.

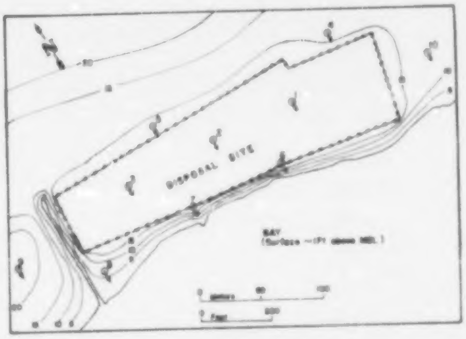
DISPOSAL SITE
BAY
N

FIGURE 4. LOCATION OF BORINGS AT SITE Z ARROWS INDICATE MOST PROBABLE DIRECTION OF GROUND WATER MOVEMENT.

to obtain soil samples at the sludge/soil interface and near or below the water table. Water samples were obtained by bailing water from the borings with a small-diameter tube lowered down the auger stem. Soil and water samples were shipped and stored under refrigeration until they could be prepared for testing or analysis.

Testing and Analytical Procedures

Soil samples were tested physically to determine water content, dry density, permeability, and grain size distribution. All testing was conducted according to standard soil engineering methods (4). Water content was determined by weighing a fresh soil sample and then drying the sample at 110°C until a constant dry weight was obtained. Sample dry densities were determined by trimming a fresh soil sample to a known volume, then drying and weighing the sample. Permeabilities were run using a constant head permeameter for coarse-grained materials and a falling-head test apparatus for fine-grained soils. Grain size analyses were conducted by passing the sample through a standard sieve set. A separate hydrometer analysis was performed on a sample passing through a 200-mesh sieve. The major characteristics of the soils or sediments, especially the grain-size analysis and the characteristics of the fine fraction were used to classify the soils into standard soil engineering categories (5).

The groundwater samples collected were filtered through a 0.45-micron membrane filter and preserved for analysis. Care was taken to store all samples under refrigeration and run the analyses within the recommended time limits (6). The techniques used for chemical analyses are given in Table 3.

TABLE 3. TECHNIQUES USED IN THE ANALYSIS OF GROUNDWATER FILTRATES

Chemical species	Procedures and/or instrumentation*	Lowest reporting concentration (ppm)
SO_4	Standard Turbidimetric Method† in combination with a Varian Model 635 Spectrophotometer	8
SO_3	Standard Potassium Iodide-Iodate Titration method†	1
Cl	Standard Mercuric Nitrate Titration Method†	5
NO_3-N	Technicon II Auto Analyzer, Industrial Method no. 100-70W‡	0.01
NO_2-N	Same as above	0.01
CN	Technicon II Auto-Analyzer, Industrial Method no. 315-75W‡	0.01
TOC	Determined with Envirotech Model No. DC 50 TOC Analyzer	1
Phenol	Technicon II Auto-Analyzer, Industrial Method no. 127-71W	<0.01
Ca	Determined with a Spectrametrics Argon Plasma Emission Spectrophotometer Model II	0.01
Fe	Determined with Perkin-Elmer Heated Graphite Automizer Atomic Absorption Unit	0.003
K	Determined with a Spectrametrics Argon Plasma Emission Spectrophotometer Model II	0.05
Mg	Same as above	0.01
Mn	Determined with Perkin-Elmer Heated Graphite Atomizer Atomic Absorption Unit	0.001
Na	Determined with Spectrametrics Argon Plasma Emission Spectrophotometer Model II	0.01
As	Determined with a Gaseous Hydride System, Perkin-Elmer Atomic Absorption Unit	* 0.001
B	Determined with a Spectrametrics Argon Plasma Emission Spectrophotometer Model II	0.02
Ba	Determined with a Perkin-Elmer Heated Graphite Atomizer Atomic Absorption Unit	0.005
Cd	Same as above	0.0003
Cr	Same as above	0.001
Cu	Same as above	0.001
Hg	Determined with a [illegible] Zeeman Shift Atomic Absorption Spectrophotometer	0.0002
Ni	Determined with a Perkin-Elmer Heated Graphite Atomizer Atomic Absorption Unit	0.005
Pb	Same as above	0.002
Se	Same as above	0.005
Zn	Same as above	0.014

* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

† Standards Methods for the Examination of Water and Wastewater, American Public Health Association, New York, 13th Edition, 1971.

‡ Technicon Industrial Systems, Tarrytown, New York.

RESULTS AND DISCUSSION

Physical Testing of Soils

Existing engineering reports had shown that at all sites selected, the soil was uniform over the area of the disposal site. The goal of the physical testing was to see if soil characteristics had been altered in the soils beneath the industrial disposal operation. Table 4 summarizes the physical testing data for samples taken directly below the fixed sludge and for samples taken at comparable depths outside the disposal site. In most cases the contrast between samples at different locations at a disposal facility was found to be very slight. A randomization test (7) was applied to the data and in only two cases were the test results found to be so extreme as to be statistically significant (93% confidence level). The water content of sediments beneath the waste at site W is significantly higher than those outside the disposal area and the percent fines (<200 mesh) in samples under the landfill site X is significantly lower than corresponding samples outside the disposal area. No consistent pattern of changes in soil character can be seen. Any changes in physical properties are occurring in the fixed waste itself, not in the underlying soil.

Chemical Analyses of Groundwater

Tables 5-8 summarize the results of the chemical analyses of groundwater samples obtained from borings at the four industrial waste disposal sites. In experimental borings through the disposal sites or downdip from the disposal areas, the concentrations of major cations and anions (Ca, Na, SO_4 and Cl) were often high suggesting contamination from the overlying waste; yet, the trace element levels were remarkably low. A randomization test (7) was used to determine which constituents were present in consistently high concentrations in either experimental or control samples. The results are summarized in Table 9.

At site W, only chloride, nitrite, calcium and sodium showed significant elevated concentrations in the experimental borings. Nitrite levels, however, were very close to the limit of detection for the analytical method used and the small variation observed does not suggest this is a major contaminant leaching from the waste. Concentrations of chloride, calcium and sodium were all well above the detection limits and the contrasts between control and experimental samples was impressive.

At site X, only sulfate, nitrate and boron showed significant differences between control and experimental samples. At this site, however, high nitrate levels

TABLE 4. COMPARISON OF PHYSICAL PROPERTIES OF SOIL SAMPLES COLLECTED DIRECTLY BENEATH AND AT COMPARABLE DEPTHS OUTSIDE THE DISPOSAL AREAS

Site	Boring no.	Position with respect to disposal area	Depth below surface (m)	Dry density (g/cc)	Water content (%)	Hydraulic conductivity (cm/sec)	%Fines*	Classification
W	1	inside	3.23 - 3.76	1.92	14.8	1.8×10^{-7}	58	Sandy clay with gravel
W	2	inside	1.40 - 1.62	1.73	16.0	2.2×10^{-6}	74	Sandy clay
W	3	outside	3.23 - 3.60	1.99	12.2	3.2×10^{-6}	58	Sandy clay with gravel
W	4	outside	0.21 - 0.43	1.75	12.8	8.8×10^{-6}	74	Sandy silt
W	5	outside	6.40 - 6.73	2.13	9.1	1.1×10^{-6}	--	Sandy clay with gravel
W	6	outside	3.76 - 3.72	1.92	13.9	5.1×10^{-7}	60	Sandy clay with gravel
W	7	outside	3.26 - 3.81	2.13	9.8	3.4×10^{-6}	34	Gravelly, silty sand
W	8	outside	6.31 - 6.52	2.05	10.1	4.0×10^{-7}	52	Clayey, sandy silt
X	1	inside	1.[illegible]6 - 1.49	1.70	20.5	3.0×10^{-8}	60	Sandy clay
X	2	inside	1.[illegible]3 - 1.77	1.56	21.7	4.5×10^{-7}	46	Sandy clay
X	3	outside	0.26 - 0.64	1.78	18.3	7.4×10^{-8}	76	Sandy clay
X	4	outside	0.21 - 0.46	1.71	18.2	2.1×10^{-7}	--	-----
X	5	outside	0.24 - 0.67	1.59	24.8	1.1×10^{-8}	63	Sandy clay
X	6	outside	0.27 - 0.46	1.88	14.5	1.4×10^{-7}	82	Silty clay
X	7	outside	0.21 - 0.58	1.81	17.4	2.2×10^{-6}	67	Sandy clay
X	8	outside	0.24 - 0.52	1.62	21.2	1.3×10^{-8}	65	Sandy clay with gravel
X	9	outside	0.24 - 0.55	1.69	20.2	2.0×10^{-8}	61	Sandy clay with gravel
Y	1	inside	0.27 - 0.64	1.73	18.6	8.3×10^{-7}	--	Clayey sand
Y	2	inside	0.21 - 0.76	1.73	17.4	1.3×10^{-6}	84	Sandy clay
Y	3	outside	1.92 - 2.44	1.75	19.5	6.4×10^{-8}	88	Clean clay
Y	4	outside	0.21 - 0.64	1.66	22.8	6.1×10^{-9}	88	Sandy clay
Y	5	outside	1.13 - 1.68	1.73	17.4	5.1×10^{-7}	42	Silty sand
Y	7	outside	1.13 - 1.68	1.57	22.1	3.4×10^{-6}	44	Clayey sand
Y	9	outside	1.16 - 1.68	1.82	17.3	1.6×10^{-6}	87	Sandy clay
Z	2	inside	4.39 - 4.72	1.48	30.5	2.2×10^{-7}	95	Plastic clay with sand
Z	3	inside	3.48 - 3.81	1.43	32.8	5.2×10^{-9}	96	Plastic clay with trace sand
Z	4	outside	3.63 - 3.99	1.45	32.0	1.5×10^{-8}	96	Plastic clay with trace sand
Z	5	outside	2.71 - 3.02	1.38	34.8	2.9×10^{-9}	96	Plastic clay with trace sand
Z	6	outside	3.32 - 3.63	1.43	31.4	---	97	Plastic clay
Z	7	outside	3.32 - 3.72	1.51	28.8	---	94	Plastic clay
Z	8	outside	2.41 - 2.80	1.60	25.4	---	95	Plastic clay

* % Fines = percent <200 mesh.

TABLE 5. CHEMICAL COMPOSITION OF GROUNDWATER OBTAINED FROM BORINGS AT SITE W

Parameters	Experimental Borings				Control Borings			
	Boring 1	Boring 2	Boring 5	Boring 6	Boring 3	Boring 4	Boring 7	Boring 8
SO_4	600	1049	299	1542	142	400	342	182
SO_3	<1	<1	<1	<1	<1	<1	<1	<1
Cl	55	50	50	26	5	15	25	20
NO_3-N	0.55	0.18	0.08	0.77	1.17	0.08	0.38	0.08
NO_2-N	0.01	<0.01	0.02	0.01	<0.01	<0.01	0.01	<0.01
CN	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	0.05	<0.01
TOC	4	32	8	12	3	8	6	2
Ca	191.00	554.00	155.00	402.00	113.00	83.10	171.00	92.80
Fe	ND	0.141	0.150	0.219	0.094	ND	0.118	ND
Mg	69.10	88.30	80.70	165.00	50.00	40.40	94.30	43.40
Mn	0.121	0.049	0.344	0.719	0.049	0.152	0.196	0.050
Na	92.10	88.90	35.70	226.00	10.90	11.90	9.80	8.50
As	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
B	0.03	0.03	0.34	4.60	0.04	0.03	0.03	0.03
Be	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Cd	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003
Cr	<0.003	<0.003	<0.003	0.003	0.003	<0.003	<0.003	<0.003
Cu	ND	ND	0.004	<0.003	0.003	ND	<0.003	<0.003
Hg	<0.0002	ND	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002
Ni	0.016	0.027	0.009	0.160	0.025	<0.005	0.009	<0.005
Pb	0.002	0.002	<0.002	<0.002	<0.002	0.005	0.013	<0.002
Se	<0.005	<0.005	0.013	0.033	0.026	<0.005	0.006	0.009
Zn	<0.014	<0.014	0.015	0.042	0.020	<0.014	0.021	<0.014

Note: All values are in mg/ℓ.

ND = Not determined.

TABLE 6. CHEMICAL COMPOSITION OF GROUNDWATER OBTAINED FROM BORINGS AT SITE X

	Experimental Borings				Control Borings				
Parameters	Boring 1	Boring 2	Boring 6	Boring 7	Boring 3	Boring 4	Boring 5	Boring 8	Boring 9
SO_4	272	502	292	262	202	ND	117	117	<8
SO_3	<1	<1	<1	<1	<1	ND	<1	<1	<1
Cl	25	35	15	25	13	ND	35	15	5
NO_3-N	0.10	1.80	0.40	0.71	18.60	ND	1.00	18.60	14.30
NO_2-N	<0.01	0.05	<0.01	<0.01	<0.01	ND	0.14	<0.01	<0.01
CN	0.05	0.12	0.04	0.04	0.05	ND	0.02	0.05	0.01
TOC	5	13	13	8	5	ND	12	7	10
Ca	40.00	82.00	116.00	113.00	94.30	83.10	66.20	88.10	99.00
Fe	ND	ND	ND	ND	ND	ND	ND	ND	ND
Mg	54.20	35.40	72.30	68.10	51.20	49.80	30.60	52.30	55.10
Mn	0.023	0.014	1.130	0.631	0.305	0.173	0.193	0.001	0.393
Na	85.00	119.00	71.10	44.40	73.30	71.90	38.20	45.50	15.60
As	<0.003	0.004	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
B	0.04	0.05	0.10	0.08	0.03	0.03	0.05	0.04	0.04
Be	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Cd	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003	<0.0003
Cr	<0.003	0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	0.006
Cu	<0.003	0.005	0.003	<0.003	<0.003	ND	<0.003	<0.003	0.005
Hg	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	ND	<0.0002	<0.0002	<0.0002
Ni	<0.005	<0.005	0.009	<0.005	0.009	<0.005	<0.005	<0.005	<0.005
Pb	<0.002	<0.002	<0.002	0.008	<0.002	0.005	<0.002	<0.002	0.002
Se	0.009	0.016	0.011	0.006	0.016	0.005	0.013	0.019	0.006
Zn	<0.014	<0.014	0.037	0.042	<0.014	0.038	<0.014	<0.014	0.014

Note: All values are in mg/ℓ.

ND = Not determined.

TABLE 7. CHEMICAL COMPOSITION OF GROUNDWATER OBTAINED FROM BORINGS AT SITE Y

	Experimental Borings					Control Borings			
Parameters	Boring 1	Boring 2	Boring 5	Boring 6	Boring 7	Boring* 3	Boring* 4	Boring 8	Boring 9
SO_4	500	950	950	500	400	1100	800	200	500
SO_3	<1	<1	<1	<1	<1	<1	<1	<1	<1
Cl	130	100	130	60	65	130	110	35	55
NO_3-N	0.04	0.24	0.01	1.60	0.20	0.05	0.13	0.19	0.16
NO_2-N	<0.01	<0.01	<0.01	<0.01	0.03	<0.01	0.02	0.01	<0.01
CN	<0.01	ND	<0.01	ND	<0.01	ND	ND	<0.01	ND
TOC	32	ND	4	ND	8	ND	ND	4	2
Ca	131.00	355.00	338.00	266.00	234.00	346.00	328.00	151.00	252.00
Fe	ND	0.336	0.107	ND	ND	0.102	0.100	ND	ND
Mg	49.80	119.00	115.00	83.60	67.30	147.00	106.00	39.20	79.60
Mn	0.137	0.550	0.410	0.006	1.270	1.07	0.707	0.827	0.377
Na	272.00	48.90	77.00	28.50	38.40	77.00	47.80	33.00	27.40
As	<0.003	0.010	0.008	0.006	0.005	0.012	0.008	0.012	0.010
B	0.06	0.05	0.04	0.03	0.04	0.07	0.10	0.04	0.05
Be	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Cd	<0.0003	<0.0003	0.0006	<0.0003	0.0004	<0.0003	0.0003	0.0004	<0.0003
Cr	<0.003	0.004	<0.003	<0.003	<0.003	0.003	<0.003	<0.003	<0.003
Cu	ND	ND	ND	ND	ND	ND	ND	ND	ND
Hg	<0.0002	ND	<0.0002	<0.0002	<0.0002	ND	ND	<0.0002	<0.0002
Ni	0.013	0.052	<0.005	<0.005	0.020	0.021	0.021	0.022	0.015
Pb	0.003	<0.002	0.003	<0.002	0.002	<0.002	0.002	0.002	0.003
Se	<0.005	0.005	<0.005	<0.005	<0.005	<0.005	0.005	<0.005	<0.005
Zn	<0.014	0.023	<0.014	<0.014	<0.014	<0.014	0.040	<0.014	0.028

Note: All values are in mg/ℓ.

ND = Not determined.

* These two borings were made in an area suspected of being contaminated by runoff from a coal storage area.

TABLE 8. CHEMICAL COMPOSITION OF GROUNDWATER OBTAINED FROM BORINGS AT SITE Z

	Experimental Borings						Control Borings			
Parameters	Boring 1	Boring 2	Boring 3	Boring 6	Boring 7	Boring 8	Boring 4	Boring 5	Boring 9	Boring 10
SO_4	24	23	158	14	79	163	<8	20	50	24
SO_3	<1	3	25	3	<1	<1	<1	<1	<1	<1
Cl	585	1500	1360	390	1010	1780	960	995	660	1630
NO_3-N	0.251	0.08	<0.01	0.13	0.02	2.35	0.01	<0.01	<0.01	0.04
NO_2-N	0.04	0.01	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
CN	0.02	<0.01	0.60	0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01
TOC	22	24	419	13	11	17	29	21	13	17
Phenol	0.06	<0.01	6.90	0.02	0.03	0.08	0.03	<0.01	0.01	0.03
Ca	206.00	349.00	241.00	161.00	362.00	354.00	226.00	277.00	175.00	294.00
Fe	0.566	11.300	ND	ND	ND	ND	ND	ND	ND	ND
K	2.80	2.00	2.70	1.20	1.80	1.50	3.00	2.30	1.00	1.10
Mg	37.50	71.70	72.70	17.60	62.40	90.50	53.50	62.40	38.00	82.90
Mn	1.230	0.622	0.103	0.542	1.050	0.049	0.030	0.155	0.408	0.201
Na	271.00	691.00	762.00	249.00	408.00	784.00	474.00	464.00	412.00	691.00
As	0.007	0.007	0.016	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
B	0.07	0.15	0.07	0.07	0.06	0.12	0.08	0.09	0.17	0.26
Be	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Cd	0.0028	0.1070	0.0056	0.0048	0.0080	0.0176	0.0078	0.0075	0.0016	0.0151
Cr	0.003	0.004	0.003	<0.003	0.003	0.003	0.003	0.003	0.005	0.005
Cu	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Hg	0.0004	<0.0002	<0.0002	0.0002	<0.0002	0.0010	0.0002	<0.0002	0.0003	<0.0002
Ni	0.014	0.028	0.191	<0.005	0.006	<0.005	<0.005	<0.005	<0.005	0.006
Pb	0.004	0.002	0.003	0.002	0.003	0.003	0.002	0.002	0.003	0.003
Se	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Zn	ND	ND	0.112	ND	ND	ND	ND	ND	ND	ND

Note: All values are in mg/l.

ND = Not determined.

were found in the control wells and not in the experimental wells. The control wells were drilled in a farmed area west and south of the disposal area and may have been contaminated by fertilizer leaching from this agricultural land. Only sulfate and boron levels increased under the fixed sludge disposal area.

At site Y, the wells that were bored on the southwest side of the sludge disposal site were in close proximity to a coal storage area for the plant boiler house. Seepage from the coal pile probably accounts for the very high sulfate levels in the two upgradient wells. The plume of contaminated water continued under the sludge disposal area making it difficult to establish which pollutants were contributed by the fixed sludge. Only boron showed a statistically significant difference in concentration between the control and experimental wells. Boron was higher in the control wells than in the experimental wells suggesting it was coming from the coal storage area, not the sludge disposal site.

TABLE 9. RESULTS OF RANDOMIZATION TEST OF CHEMICAL ANALYSES OF GROUNDWATER SAMPLES

Chemical constituent	Site W	Site X	Site** Y	Site Z
SO_4	NS	S	NS	NS
SO_3	--	—	--	S
Cl	S	NS	NS	NS
NO_3-N	NS	S	NS	NS
NO_2-N	S	NS	NS	S
CN	NS	NS	ND	S
TOC	NS	NS	ND	NS
Phenol	NS	ND	ND	S
Ca	S	NS	NS	NS
Fe	ND	ND	ND	ND
Mg	NS	NS	NS	NS
Mn	NS	NS	NS	NS
Na	S	NS	NS	NS
As	--	--	NS	S
B	NS	S	S	NS
Be	--	—	--	—
Cd	--	—	NS	NS
Cr	--	—	NS	S
Cu	--	NS	ND	ND
Hg	--	—	--	NS
Ni	NS	—	NS	NS
Pb	NS	NS	NS	NS
Se	NS	NS	NS	--
Zn	NS	NS	NS	ND

** Data from experimental borings tested against data from upgradient borings only.

— = Too few samples above detection limit.

NS = Not significant at 94-96% level.

S = Significant at 94-96% level.

ND = Too many samples not determined.

At site Z, the sludge disposal area is between a tank farm and a small brackish bay. The combination of these circumstances results in high background levels of many constituents in the groundwater. The randomization test indicated the occurrence of significantly higher levels of sulfite, nitrite, cyanide, phenols and arsenic in the experimental wells. The concentrations of chromium observed also were significant statistically; however, the levels of chromium observed were very close to the limit of detection for the analytical technique used and the chromium levels were higher in the control borings than in the experimental borings. The fixed sludge contained a great deal of oil and the groundwater samples from under the disposal area smelled strongly of oil and phenol. The decomposition of these oily materials may account for the production of sulfite and nitrite, as well as, the persistence of cyanide that may have been present in the refinery sludge. The phenols and arsenic are probably migrating directly from the fixed sludge.

Table 10 summarizes the groundwater analyses on the basis of occurrences of certain constituents at levels that exceeded standards for public water supplies (8). The control wells in many cases contained unacceptable levels of pollutants as might be expected in areas of constant industrial activity. In only a few cases could contaminants be detected at unacceptable levels in experimental wells that did not also appear at elevated levels in control wells. These cases include the occurrence of boron at site W, sulfate at site X, iron at site Y and cyanide at site Z.

CONCLUSIONS AND COMMENTS

Physical Properties

The physical properties of soil samples from beneath the stabilized industrial sludges did not appear to be notably different from soil samples collected at similar depth in the surrounding area. The disposed material may itself have altered physical properties; but, there is no indication of any effect on underlying soils.

Chemistry of Groundwater Samples

Changes in groundwater quality attributable to sludge disposal could be observed in three of the four sites investigated. At one of the two auto assembly plants, the levels of chloride, calcium and sodium showed significant increases under and down the groundwater gradient from the disposal site. At the electroplating facility, sulfate and boron levels increased under and down the groundwater gradient from the disposal site. At the disposal site for stabilized refinery sludge, increased levels of sulfite, nitrite, cyanide, phenols, and arsenic were found in water samples taken under and down the groundwater gradient from the disposal sites.

With the exception of phenols at site Z, none of the toxic constituents predicted to be pollution problems on the basis of analysis of the waste material (Table 1) were found in significantly elevated concentrations in the groundwater. The absence of these pollutants may be attributable to lack of time for transport of these materials to the groundwater, attenuation effects occurring in the soils, or binding of these constituents in the fixation/stabilization process. Future work in this project will concentrate on analyses of nitric acid digests and distilled water leaches of soils in and around the disposal sites to establish metal levels in the soil as an indication of contaminant attenuation.

TABLE 10. OCCURRENCES OF CONCENTRATIONS OF CONSTITUENTS IN GROUNDWATER ABOVE STANDARDS FOR PUBLIC WATER SUPPLIES

Chemical constituents	Site W		Site X		Site Y		Site Z	
	Control borings	Experimental borings	Control borings	Experimental borings	Control borings	Experimental borings	Control borings	Experimental borings
SO_4	2	4	0	4	2	5	4	6
Cl	0	0	0	0	0	0	0	0
NO_3-N+NO_2-N	0	0	0	0	0	0	0	0
CN	0	0	2	2	0	0	0	1
Phenols	ND	ND	ND	ND	ND	ND	3	5
Fe	0	0	ND	ND	0	1	ND	2
Mn	3	3	4	2	2	4	3	5
As	0	0	0	0	0	0	0	0
B	0	1	0	0	0	0	0	0
Cd	0	0	0	0	0	0	1	2
Cr	0	0	0	0	0	0	0	0
Cu	0	0	0	0	ND	ND	ND	ND
Hg	0	0	0	0	0	0	0	0
Pb	0	0	0	0	0	0	0	0
Se	2	1	2	2	0	0	0	0
Zn	0	0	0	0	0	0	ND	ND
No. borings sampled	4	4	5	4	2	5	4	6

ND = Not determined.

ACKNOWLEDGEMENTS

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LAND CULTIVATION OF INDUSTRIAL WASTES

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ABSTRACT

Among the land disposal methods available for industrial wastes, land cultivation has been practiced by pharmaceutical, tannery, food processing, paper and pulp, and oil refinery industries, and offers an acceptable means of disposal for other organic wastes as well. The soil environment can assimilate most types of industrial organic waste by processes of adsorption, dilution, biodegradation, and oxidation. The main objectives of this study were to gather and assess available information on land cultivation of industrial sludges with emphasis on characterization of waste types, quantities, operational technology, economics and environmental impacts. This paper summarizes results from a state-of-the-art investigation over a 20-month period.

INTRODUCTION

The land cultivation method of disposal involves several steps: (1) application of waste onto the surface soil, (2) mixing the waste with the surface soil to aerate the mass and expose waste to soil microorganisms, (3) possibly adding nutrients or other soil amendments, and (4) remixing the soil/waste mass periodically to maintain aerobic conditions. This disposal method is also referred to as landspreading, land farming, soil incorporation, sludge farming, and other names.

Land cultivation is being more widely practiced as one alternative to conventional or unacceptable waste disposal techniques. However, very little published data are available on the land cultivation method, its benefits, disadvantages, and potential environmental impacts. Accordingly, the U.S. Environmental Protection Agency, Solid and Hazardous Waste Research Division, Municipal Environmental Research Laboratory, sponsored a comprehensive state-of-the-art study of the land cultivation practice.

The project has several basic objectives:

- Document the extent of land cultivation use and project the future use
- Identify waste types amenable for disposal by land cultivation
- Evaluate actual or potential impacts from land cultivation
- Assess status of state regulations relevant to land cultivation activities
- Prepare a conceptual design for a hypothetical land cultivation disposal site

- Estimate costs to implement and operate a site.

Information sources included personal interviews, published and unpublished literature, and case study investigations. The project is completed and final report publication is expected in mid-1978. This paper presents a summary of report findings concerning industrial wastewater and sludge disposal. A companion paper on land cultivation of municipal solid waste is published in the Proceedings of the Third Annual Municipal Solid Waste Research Symposium (1).

LAND CULTIVATION - AN ALTERNATIVE TO CONVENTIONAL LAND DISPOSAL

Soil is a natural environment for the deactivation and degradation of many waste materials through complex physical, physiochemical, chemical, and microbiological processes (2). Land cultivation of waste is a disposal technique by which wastes are mixed with the surface soil to promote these processes, particularly microbial decomposition of the organic fraction. If managed properly, the process could be carried out repeatedly on the surface of a disposal site. In practice, sludges are either hauled directly from the wastewater treatment plant or from an interim storage lagoon to the disposal site. The sludges are applied to the land by spraying, spreading, or subsurface injection. The field is then disced or plowed by conventional farm cultivation equipment.

Proponents of land cultivation claim that the site could be returned to any other land use, including agriculture, after cessation of disposal activities. Possible disadvantages of land cultivation include the need for relatively large tracts of land, long-term exposure of wastes to the atmosphere, and impacts on vegetation grown at the site.

The potential merits of land cultivation have encouraged many industries and waste disposal contractors to implement full or pilot scale operations. Many more industries are studying the concept. Results of this study point to the potential applicability of land cultivation as a disposal alternative to conventional sanitary landfill, incineration, and ponding for certain waste types, although the method is not a panacea for industrial waste generators.

WASTES SUITABLE FOR LAND CULTIVATION

Table 1 lists those industries that produce wastes considered amenable for land cultivation. The suitability of an industrial waste for land cultivation depends on such characteristics as concentrations of chemical constituents in the soluble as well as insoluble forms; bulk densities of waste solids; pH, sodium, and soluble salt contents; as well as flammability and volatility (3,4). Local climatic conditions can influence the viability of this disposal practice. Excessively high moisture content may impede oxygen transfer to soil microorganisms, thereby slowing waste degradation. Also, it is operationally difficult to mix waste into a muddy soil. Establishment of a vegetative cover can enhance the disposal practice through the uptake of any excess nutrients and water. Lacking specific information, the Irrigation Water Quality Criteria (5) and existing proposed guidelines of heavy metal loading for sewage sludges can be used as a first approximation to determine the suitability of industrial wastewaters and sludges for land cultivation (4).

TABLE 1. WASTES AMENABLE
TO LAND CULTIVATION

- Food and kindred products
- Textile finishing
- Wood preserving
- Paper and allied products
- Organic fibers (noncellulosic)
- Drugs
- Soap and detergents
- Organic chemicals
- Petroleum refining
- Leather tanning and finishing

Industrial Wastewaters

Land cultivation of wastewaters from food processing, pulp and paper, textile, tannery, wood preserving, and pharmaceutical industries has been practiced on a limited scale (6). At most locations, the practice is primarily used as a wastewater treatment method, and little or no effort has been made to incorporate wastewater into the soil.

Three application methods are generally used: overland flow, slow infiltration, and rapid infiltration (7). It appears that of the three methods, slow infiltration through spray irrigation offers the highest degree of disposal reliability and potential for long-term site usage. Overland flow may require operational manipulations to realize the same useful site life as slow infiltration. Rapid infiltration or groundwater recharge requires extensive and thorough subsurface site investigations to ensure that favorable conditions exist.

Industrial Sludges

The information gathered indicates that industrial sludges applicable to land cultivation have been either organic (e.g., oil refinery, paper and pulp, and fermentation residues), or treated inorganic (e.g., steel mill sludge) wastes containing low concentrations of extractable heavy metals. When the sludge is applied to agricultural land, it is sometimes used as a soil amendment to improve soil characteristics and/or low-analysis nitrogen fertilizer, although straight disposal is usually the prime goal.

Among the industrial sludges, oil refinery wastes have been most extensively disposed of by land cultivation (8,9). Oil degradation rates vary, depending on climate, oil content in the soil, and fertilization. The types of oily wastes that are disposed by land cultivation include cleanings from crude oil, slop emulsion, API separator bottoms, drilling muds, and other cleaning residues (9). The sludge is spread to a depth of about 7 to 20 cm by a track-dozer, and then disced into the soil. At existing sites, mixing intervals vary from once per week over several weeks to twice per year. The practice is strictly for disposal; no crops or vegetation other than weeds grow at the sites.

Some industries and disposal firms are practicing land cultivation of hazardous industrial sludges on a trial basis. In most instances, the sludges have been pretreated to inactivate or remove the hazardous constituents in the waste.

Waste Loading Rates

Loading rates generally depend on the waste's BOD, total dissolved solids, heavy metal and soluble salt contents, and the soil's texture and drainage characteristics. Table 2 indicates that wastes with a wide range of chemical characteristics have been land cultivated without apparent problems.

TABLE 2. CHARACTERISTICS OF LAND CULTIVATED WASTES

Parameter	Maximum Concentration/Value
BOD	5,000 ppm
COD	18,000 ppm
SS	3,000 ppm
TDS	4,000 ppm
pH	2 - 12

Most state regulations do not presently control application of waste to soil based on the concentration of heavy metals or other potentially toxic constituents contained in the sludge. Increased regulation will likely occur, as land cultivation becomes more common. Overall, the Sanitary Landfill Criteria promulgated by EPA for application to all land disposal facilities will apply to land cultivation operations.

As noted, soil can often serve as an effective disposal sink for industrial wastes. However, if a soil cannot assimilate the applied waste, it will become anaerobic, resulting in nuisance conditions and failure of the system to effectively degrade the organic matter. Furthermore, unless the wastes are detoxified or decomposed by the soil or weather to nondeleterious products, the upper soil zone receiving the wastes eventually could become loaded to its ultimate capacity. As a result, disposal activities at the site will have to be terminated and the site may be unusable for alternative purposes for many years.

Volume of Waste Suitable for Land Cultivation

Figure 1 shows the estimated volume of both industrial sludge and wastewater that were suitable for land cultivation in 1975. Projected volumes for 1980 and 1985 are also indicated. These wastes represent approximately 3 percent of all industrial sludge and wastewater generated and projected for generation in the United States. Thus, while the method could accommodate specific waste streams, land cultivation

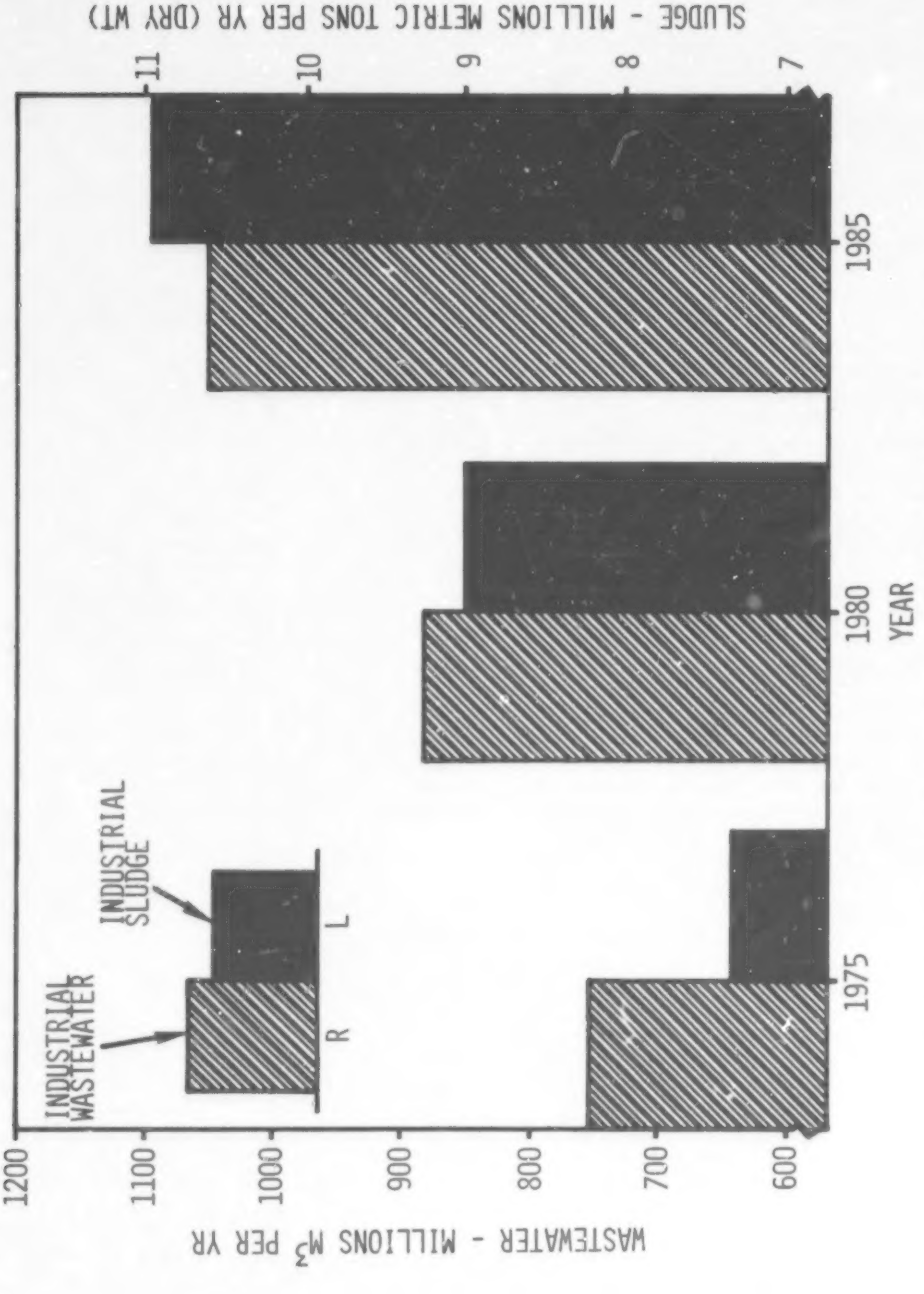

Figure 1. Volumes of industrial waste suitable for land cultivation.

will not significantly decrease the overall demand for other industrial waste disposal methods.

ENVIRONMENTAL IMPACTS

Data concerning environmental contamination from industrial waste land cultivation are scarce. Improper land disposal of industrial wastes often goes unnoticed in the short term because the impacts are chronic, rather than acute (10). Buried potentially hazardous compounds may move slowly and take decades to leach through soil into surface and groundwater supplies (10). Similarly, environmental impacts of land cultivation operations may not be readily detectable at first application and mixing. When waste is incorporated into the surface soil, it triggers a series of physical, chemical, and biological processes. Phillips and Nathwani (2) have reviewed the various mechanisms involved in soil-waste interactions. Of significance are the potential impacts on ground and surface water, air quality, soil, vegetation, and human and animal health.

Water Quality Impacts

Wastes applied to surface soils are susceptible to washout by precipitation runoff. Land cultivation designs generally include appropriate drainage control facilities to prevent such occurrences, including upstream runoff diversion channels and holding ponds or settling basins to contain any waste-laden runoff water from precipitation incident on the site. No evidence of surface water contamination due to runoff from a land cultivation site is documented although flooding has been reported. Flood problems are due to poor site selection rather than inherent shortcomings of the disposal method itself.

As with any land disposal operation, groundwater quality may be impaired if surface-applied waste constituents move through the subsurface soil to underlying aquifers. Soils exhibit tremendous chemical and biological attenuation and degradation capacity due to their high reactive surface area and the available varied microbial populations. However, if a waste has soluble or partly soluble constituents, there is always a risk that it will affect the quality of subsurface waters. For example, Adriano, et al. (11) have shown that the nitrate and phosphate levels in subsurface waters exceeded public health standards and environmental guidelines, respectively, from long-term land treatment of food processing wastewaters.

The downward movement of heavy metals, oils, and pesticides in soils is often restricted, due to low water solubility, and high retention and degradation by various soil processes (9,12,13). Other chlorinated hydrocarbons, phenols, and detergent components may be present in varying amounts in the wastes, mostly depending on the generator industry. It is believed that such organic compounds will be eventually decomposed by soil microorganisms. Precise decomposition times are not known. Unless the soil is overloaded with wastes containing large amounts of these substances, land cultivation is not likely to pose a serious threat to groundwater quality.

Air Emissions

Like municipal effluents and sludges, certain industrial wastewaters and sludges can also emanate odors when exposed to the atmosphere, impairing air quality of the disposal area. If the waste contains volatile components, land cultivation practices could increase evaporation of these components, although much of the readily volatile fraction would have come off during waste handling prior to delivery to a disposal site. Additionally, during soil incorporation, dust could present a health hazard to the personnel on the site and may be carried off site by winds. Subsurface injection of the waste and/or mixing with soil as soon as practical after deposition can alleviate, but not always eliminate, odor and evaporation problems.

Soil Impacts

As part of this study, composite samples of surface soil and typical native vegetation were taken from several land cultivation sites. Samples were also collected from the corresponding control sites which had similar soil and vegetation, but had received no waste. The objective of the limited sampling program was to determine the effect of land cultivation on soil chemical properties and elemental uptake. Pertinent information on two of the sites studied is presented on Table 3. Note that the site age, soil, and sludge characteristics from the two sites are markedly different. Site A is managed by

TABLE 3. PERTINENT INFORMATION ON STUDY SITES USED IN THE INVESTIGATION OF VEGETATIVE IMPACTS OF LAND CULTIVATION

	Site A	Site B
Area of site	14 ha (35 ac)	8.2 ha (20 ac)
Waste type	Drilling muds Tank bottoms	API oil/water separator sludges
Waste volume	1,000 to 1,200 bbl daily	Periodic disposal, 185,000 bbl/year
Soil Characteristics	Sandy, well-drained, slightly acidic	Clayey, poorly drained, alkaline
Depth of soil/waste mixture	0.9 to 1.2 m (3 to 4 ft)	15 to 30 cm (6 to 12 in)
Site age	22 years	5 years
Vegetative type	Weeds and shrubs are growing along the perimeter of the disposal area	Same as Site A
Vegetation sampled	Tall grass, golden bush, ragweed, and ice plant	Nut grass leaves and cocklebur seeds

TABLE 4. CHEMICAL CHARACTERISTICS OF THE SURFACE SOILS FROM CONTROL AND OIL-TREATED PLOTS

	Site A		Site B	
Constituents*	Control	Treated	Control	Treated
pH	6.04	7.65	7.41	7.40
EC, mmhos/cm	0.40	4.46	2.21	3.91
Oil, %		2.28		2.06
TKN, %	0.006	0.079	0.080	0.134
Org. C, %	0.16	2.53	2.10	5.10
	-------- ppm	--------	-------- ppm	--------
P	410	230	17.5	17.5
Na	110	280	185	375
B	0.2	2.28	0.2	0.22
Mn	5.4	55.0	65	71.6
Ni	1.5	2.5	4.8	5.3
Zn	7.5	40.7	53.5	71.5
Se	0.022	0.09	0.01	0.028
Mo	1.3	1.1	0.6	0.55
Cd	0.14	0.06	0.06	0.06
Pb	4.2	5.4	212	242

[*] Electrical conductivity (EC) and B were measured in the saturation extracts; other elements in ppm were determined in 0.1N HCl extracts.

a disposal company, whereas Site B is located within and managed by an oil refinery plant.

Results of soil analyses (Table 4) show that land cultivation of oily wastes at Site A resulted in increased pH, soluble salt content (expressed as EC), and levels of total Kjeldahl nitrogen (TKN) and organic carbon in the sandy soil. Likewise, water-soluble B and 0.1N-extractable Na, Mn, Ni, Zn, Se, and Pb also increased. At Site B, similar increases were noted for soluble salts, TKN, organic carbon, and 0.1N-extractable Na, Mn, Zn, Se, and Pb. Except for Pb concentrations at Site B, the elements analyzed had concentrations which are within the range typically found in soils.

Impacts on the Food Chain

The most significant potential human health impact is uptake of waste constituents by vegetation and subsequent ingestion of such vegetation by animals and/or humans.

At ongoing industrial wastewater land treatment sites, a cover crop is generally regarded as an integral part of the system, useful to improve water infiltration, remove nutrients, and increase the allowable hydraulic loading. In disposing of industrial sludges by land cultivation, existing vegetation is usually removed from the site before waste application. Weeds and small bushes will become established in the disposal plot only if the plot is left untilled for some time. Available information indicates that crops grown on agricultural soils treated with selected industrial wastewaters and sludges do not accumulate toxic metals in sufficient quantities to adversely affect plant growth. However, long-term effects of land cultivation on crop quality and the food chain are not known.

Land cultivation of wastes can pose hazards to the food chain through surface contamination and plant uptake. For example, pesticide residues have been shown to accumulate in various crops by these mechanisms (14), rendering the crops unsafe for consumption.

The effects of potentially toxic elements in sewage sludges and effluents on the food chain have been discussed in the literature. Cadmium, Cu, and Zn are the elements commonly posing significant potential hazards to the food chain through plant accumulation (15). However, it should be noted that under improper site management (overloading, low pH, etc.), elements such as Pb, Hg, As, Se, Mo, and Ni, if present in significant quantities in the wastes that are land cultivated, could also pose serious hazards to man and animals consuming the crops.

Limited data are available from greenhouse and field investigations conducted to evaluate the potential adverse effects of application of some industrial sludges on the yield and quality of crops. DeRoo (16) evaluated the use of mycelial sludges produced by the pharmaceutical industry in Connecticut as a nitrogen fertilizer and organic soil amendment. He concluded that if the mycelial sludge is applied repeatedly at high rates (222 mt/ha) to the same field, the soluble salt concentration and high zinc content in the sludge may be injurious to plants. Studies with similar objectives have been conducted using lagooned paper pulp sludge (Jacobs, personal communication), cannery fruit sludge (17), and nylon sludge (Cotnoir, personal communication). Results indicated that these sludges would have value as a low-analysis nitrogen fertilizer, and that no adverse effects were observed in crops and soils.

In field studies, the effects of a refractory metal sludge (18) and steel mill sludge (Nelson, personal communication) on the yield and chemical composition of forage and grain crops were evaluated. No adverse effects from heavy metals were observed. In the case of steel mill sludge, the growth was stunted at high waste application rates (sludge about 20 cm thick), which was attributed to nitrogen and phosphorus deficiencies and poor aeration from soil compaction. A thorough survey and chemical analysis of all types of vegetation at the 10 case study land cultivation sites was not possible within the project scope. Some typical and prevalent species were sampled and analyzed, as highlighted in Table 5, which summarizes data from Sites A and B.

Results from these plant analyses indicate differences in plant uptake due to differences in site conditions, plant species, and waste oil treatment methods. At Site A, ragweed and ice plant grown on the oil-treated plot contained higher

TABLE 5. SELECTED RESULTS OF VEGETATION ANALYSES AT TWO CASE STUDY SITES

Element	Site A*				Site B*			
	Ragweed		Ice Plant		Nutgrass		Cocklebur Seed	
	C	T	C	T	C	T	C	T
	---- % ----		----- % -----		----- % ----		-------- % --------	
N	2.52	0.87	1.29	0.91	1.44	1.42	3.05	1.07
P	0.32	0.33	0.21	0.21	0.17	0.11	0.29	0.16
	--- ppm ---		---- ppm ----		---- ppm ----		------ ppm ------	
Na	2560	3375	20937	36560	2062	6187	1000	687
B	102	96	12	12	7	15	28	14
Mn	88	95.4	96.7	198	63.6	48.7	18.8	19.1
Ni	6.9	8.5	3.8	2.0	1.9	6.3	3.6	3.1
Zn	101.4	190	40.6	38.2	93.8	131.9	43.8	53.1
Se	0.04	0.125	0.04	0.04	0.23	0.23	0.04	0.04
Mo	1.2	0.71	0.31	< 0.1	7.1	9.5	4.2	8.7
Cd	0.05	0.05	0.10	0.21	0.41	0.41	0.15	0.15
Pb	3.12	18.0	3.12	3.28	61.5	90.5	11.2	23.2

*C = control plot, T = treated plot

concentrations of Na, Mn, Zn, Se, and Pb than those from the control plot. These observations related to the trends in soil data. Plant N contents were reduced by the land cultivation treatment, probably due to immobilization of available N by the soil microorganisms. This suggests that nitrogen fertilizer application may be necessary for an oily waste disposal area if subsequent growth is planned.

Nut grass and cocklebur grown on the oil-treated plot from Site B contained higher concentrations of Zn, Mo, and Pb than those grown on the control plot. Overall, concentrations of the elements analyzed were lower in the cocklebur seed than the concentrations in nut grass. The levels of Mo and Pb in both plant species from the oil-treated plot are worthy of notice since they have approached the undesirable level (≥ 10 ppm) for animal consumption. The concentrations of Pb were exceedingly high, comparable to the Pb concentrations in pasture grasses in a lead-contaminated area near Antioch, California (Ganje, personal communication). The data suggest that nut grass and cocklebur have accumulated significant amounts of Pb, particularly from the oil-treated plot.

Humans and other animals can also be affected by land cultivation waste disposal practices in other ways. For example, site workers could be injured by contacting deleterious wastes; unauthorized visitors could inadvertently contact the waste; and dust or fumes laden with possibly hazardous concentrations of toxic chemicals, heavy metals, or pathogens due to waste application may move off site to settle on nearby untreated fields. Also, poorly operated land cultivation sites may be aesthetically unpleasing. These and other adverse impacts are possible, but no such health threatening incidents have been documented.

LAND CULTIVATION ECONOMICS

Figure 2 shows the unit costs of industrial liquid and sludge waste disposal for five case study sites. Also shown is the expected range of costs for a hypothetical land cultivation site, estimated on the basis of conceptual designs prepared during the project. Unit cost values for both actual case studies and the conceptual design include expenditures for land, equipment, labor, interim on-site storage of waste, and environmental monitoring. Costs

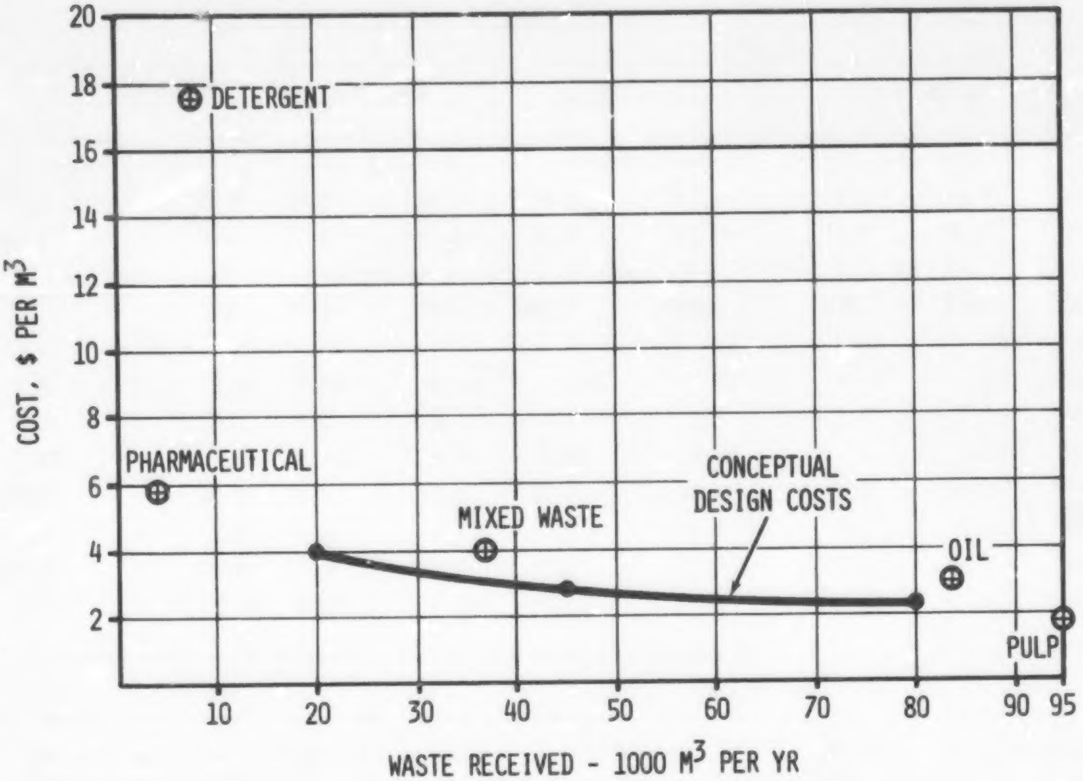

Figure 2. Costs of hypothetical conceptual design for a land cultivation site compared to case study costs.

for waste transport to the site are not included.

Capital costs for the conceptual design ranged from \$262,000 to \$746,000 for waste delivery rates from 1,000 to 4,000 dry metric tons per year (equivalent to 5,340 to 21,370 gal per year of sludge @ 5 percent solids).

Costs for disposal of uncontained industrial wastes by sanitary landfill methods generally range from \$5.30 to \$22.00 per m^3 (\$0.02 to \$0.08 per gal), depending on location, site volume, and other factors. For industrial waste disposed of in drums or other containers, costs can be substantially higher, ranging up to \$194 per m^3 (\$0.72 per gal). Thus, land cultivation cost is comparable with or lower than conventional disposal methods.

MONITORING

A monitoring program for a land cultivation facility is best tailored to specific waste and site conditions encountered. If volatile wastes are to be handled, air emissions should be monitored. Any crops for human or animal consumption grown on waste-treated soil should be periodically analyzed to ensure that potentially harmful levels of contaminants are not building up in edible portions of plant tissue.

Monitoring for groundwater quality control may be simpler and less costly at a land cultivation site as compared to a sanitary landfill. Since wastes are applied only to the surface soil, routine analysis of surface and near-surface soil samples can indicate if and when any contaminants are moving away from the zone of waste incorporation. Any movement of contaminants can be detected and remedial action taken well before groundwater has been contaminated. Monitoring groundwater via wells is generally not necessary except to establish background water quality data prior to site activation.

SUMMARY AND RECOMMENDATIONS

Industrial wastewaters and sludges that have been land cultivated are primarily from food processing, oil refinery, paper and pulp, tannery, and pharmaceutical industries. The wastes are composed mainly of organic material and are thus biodegradable. The land cultivation practice is limited and will likely remain in applicability to about 3 percent of all industrial wastes. Land cultivation is viable only where soil, climate, waste characteristics, and environmental conditions permit. Depending on specific conditions, the disposal program can either be related to agriculture or can be solely a disposal practice.

Existing state regulations generally call for consideration of planned land cultivation projects on a case-by-case basis. However, with increasing use of this disposal method and in light of new EPA criteria that include coverage of land cultivation activities, many states will likely implement specific regulations.

Documented environmental impacts of land cultivation operations concern loading soil with waste constituents, plant uptake of heavy metals, and emanation of odors. These and other potential impacts are controllable by improved operating techniques and effective monitoring programs. In particular, routine soil monitoring to detect any movement of waste constituents away from the zone of incorporation can provide an early warning of fugitive contamination. In the face of a substantial threat to groundwater, all land cultivated waste at a site could be removed to other sites.

Land cultivation costs are in the range of \$2 to \$18 per m^3 (\$0.01 to \$0.07 per gal) of industrial waste, varying with waste type, loading rates, site usage, site area, and other factors. These costs are generally competitive with other methods of industrial waste disposal.

Recommendations developed on the basis of this study include:

1. All wastes should be routinely analyzed before and during land cultivation operations to ensure that an accurate record of applied material is developed. If potentially deleterious or incompatible waste is delivered for disposal, it should not be accepted.
2. As for all land disposal facilities, a site for land cultivation should be carefully selected to afford maximum environmental protection.
3. An engineering design for a land cultivation site should be prepared to ensure provision and proper configuration of runoff control, facilities, access roads, waste storage facilities, personnel safety features, and equipment maintenance sheds.
4. A specific protocol for waste receipt, spreading, mixing, remixing, monitoring, and trouble shooting should be developed and followed as an integral part of land cultivation operations.
5. A monitoring program is essential. Routine soil monitoring wherein surface and subsurface soils are analyzed for presence of waste constituents can detect any movement of contaminants toward groundwater. Air monitoring may also be necessary.
6. Further research is warranted into such topics as waste degradation mechanisms, fate of degradation products, soil retention potential, limits of waste loading in soils, and air quality impacts of land cultivation.

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COST ASSESSMENT FOR THE EMPLACEMENT OF HAZARDOUS MATERIALS IN A SALT MINE

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ABSTRACT

The results of an economic evaluation of storing non-radioactive hazardous wastes in a room and pillar type salt mine are discussed. The results include capital and operating costs, and a cost analysis. The cost study was based on a simulated waste characteristic and conceptual design of the waste receiving, treatment, containerization, and underground storage facilities. The storage facilities were designed for long-term storage of hazardous wastes in solid form and in an environmentally safe manner. The cost of storing hazardous wastes in a salt mine depended considerably on the system capacity, the waste characteristics, and the storage methods.

INTRODUCTION

The promulgation of air and water pollution control regulations has resulted in more effective removal of contaminants from waste streams, especially the hazardous constituents in many industrial effluent streams. These cleanup activities have resulted in an increased quantity of concentrated hazardous wastes that must be disposed of. Disposal of hazardous wastes in a manner that isolates them from the environment is becoming a difficult problem throughout the country.

In a continuing effort to find a new and improved method of disposing of or storing hazardous wastes, EPA has been supporting a number of studies on the hazardous waste disposal, including offshore incineration, secured landfill, chemical stabilization, encapsulation, and isolation.

One of these studies was "Evaluation of Hazardous Wastes Emplacement in Mined Openings" (EPA-600/2-75-040), supported by the Solid and Hazardous Waste Research Division (SHWRD) of the Municipal Environmental Research Laboratory, EPA(1). The study, conducted by Fenix and Scisson, Inc., provided an assessment of the technical feasibility and environmental acceptability of emplacing hazardous industrial wastes in underground mines. The study concluded that storing hazardous industrial wastes in a room and pillar type salt mine would be an environmentally acceptable method of managing hazardous waste, provided that the recommended procedures of site selection, treatment, containerization, and waste handling are followed. In view of this assessment EPA decided that an economic evaluation of the concept should be conducted. This economic evaluation is the subject of this paper.(2)

The objective of this study then was to provide EPA with the necessary cost information to make sound decisions on future commitments of resources regarding the emplacement of hazardous wastes in underground storage facilities.

The study involved four major tasks:

(1) Development of Design and Operating Criteria
  - Typical salt mine
  - Characteristics of received waste
  - Characteristics of stored material
  - Required treatment

(2) Conceptual Design
  - Surface facility
  - Subsurface facility

(3) Cost Estimates
  - Capital costs
  - Operating costs

(4) Economic Analyses of Overall Operation

DESIGN BASIS OF THE STUDY

The only known practice of underground storage of hazardous wastes is at Herfa-Neurode in West Germany. At the present time, that operation is a simple storage facility without treatment or recontainerization of received wastes. No attempt is made to convert the wastes to a more stable form. It was decided that for this study, a fresh approach based on the trend of U.S. waste management practices would be developed.

The characteristics of hazardous wastes to be received, waste treatment and containerization, and storage concept used in this study reflect the current U.S. hazardous waste management practice and its likely future changes.

Waste Characteristics

It was apparent from the literature that at the present time the characterization and inventory of hazardous wastes are incomplete. It is also expected that the characteristics of hazardous wastes (i.e., both quantity and composition) will be changed rapidly as new laws and new management programs are implemented.

From these findings, it was concluded that the hazardous waste characteristics to be used for this study would be of a general nature, reflecting a wide range of waste types, but specific enough to reveal the requirements of different treatment and handling methods.

The hazardous wastes were classified into four groups, each of which requires different treatment and handling. These waste types are defined as follows:

- Type A. Aqueous liquids and slurries containing dissolved hazardous elemements, primarily toxic heavy metals. Type A wastes require chemical treatment before dewatering, containerization, and storage. Type A wastes include four subtypes: chromate waste (A-1), cyanide waste (A-2), acid/caustic waste (A-3), and nonreactive waste (A-4).
- Type B. Aqueous and organic sludges containing solid hazardous elements. Type B wastes require only pH adjustments and dewatering before containerization and storage. Type B wastes include acid/caustic sludges (B-1), inorganic sludges (B-2), and organic sludges (B-3).
- Type C. Inorganic and organic solids containing solid hazardous elements requiring only containerization before storage.
- Type D. Special wastes to be stored on a temporary basis at customer request. These wastes will be retrieved and sent back to the waste generator. This is included to develop cost data associated with short-term storage of the waste and its retrieval.

Study Mine

One of the study tasks was to evaluate existing salt mines to select one specific typical salt mine suitable for the storage of hazardous waste. The selected mine was used as a base from which design and cost information were obtained. To prevent potential adverse public reaction, the study mine has not been identified. Due to the limited time and budget, the selection procedure was to be based on readily available information without actual site surveys of the mines being considered.

Seventeen salt mines were considered. Based on the preliminary evaluation, three mines were considered acceptable for storing hazardous waste without any extensive mine rehabilitation. Any one of the three mines could have been selected as a typical salt mine acceptable for the storage of hazardous waste. However, one of them had more available information, and with the approval of the EPA Project Officer, this mine was selected for the study.

General Description - -

The selected mine is conveniently located near a major metropolitan area with a heavy industrial output. Direct access to the mine is provided by several railroads and interstate highways.

Mining of the selected mine began over 50 years ago in a bed of salt at a depth of approximately 1,400 feet. The seam thickness ranges from 25 to 30 feet. The ongoing monitoring program has established that the mine is stable, and there have been no significant changes in the mine environment since the initiation of mining. Two shafts provide access to the mine. The production shaft is a 16-foot diameter, concrete-lined shaft divided into four compartments, two hoisting compartments, each with a 10 ton capacity, and two service compartments. The second shaft, a man and service shaft, is a 4- by 8-foot rectangular, concrete-lined shaft, divided into two compartments.

The mining method is conventional room and pillar. Rooms of 60 feet wide with a ceiling height of from 18 to 27 feet are mined at the end of a long gallery, up to several thousand feet long. At regular intervals along the gallery are huge pillars of rock salt 60 by 80 feet, which are the sole means of supporting the roof. Using this system, about 65 percent of the salt is extracted. Several feet of salt are left to preserve the roof and several inches to preserve the floor.

To get a better perspective of the size of room and pillar mines, Figure 1 presents a photo of a main haulway in a mine. The

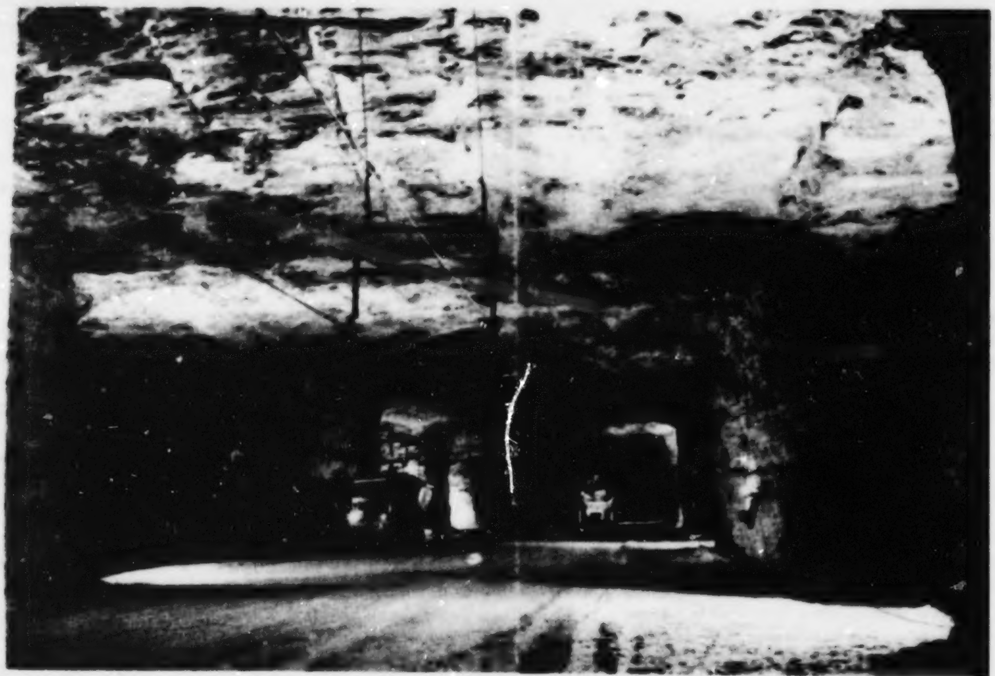

Fig. 1 Main haulway in a salt Mine (courtesy of Int. Salt Co.)

pillars are visible on either side of the haulway. Figure 2 illustrates the typical room and pillar arrangement. Conditions are a comfortable 58°F year round with a relative humidity of 55-56 percent.

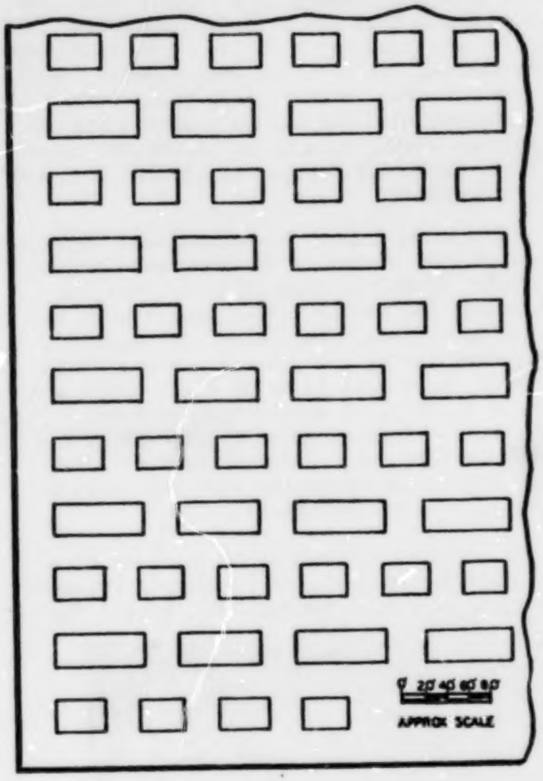

Fig. 2 Typical room and pillar arrangement

Mine Facilities --

Surface -- Surface facility includes the offices, warehouses, shops, and salt processing plant. In addition, there are complete truck and rail loading and unloading facilities.

Underground -- The mine itself contains very little in the way of permanent facilities. The area adjacent to the main shaft has been developed to serve as a shelter in case of a mine fire. Other facilities in the mine include an office, a machine shop, water tanks, and the pump facilities. All other mine facilities are of a temporary nature and are frequently relocated as the production areas change.

Available Storage Space --

The general mine layout is shown in Figure 3, with mining currently taking place in one area.

An upper limit on the storage space in the mine has been estimated from production figures and mine maps. This, however, reflects the void left by mining and must be reduced to reflect actual conditions in the mine.

The total open space in the mine designated for the waste storage is estimated to be 500,000,000 cubic feet. This is located in the following areas as designated in Figure 3.

Area	Cubic Feet
X_1	210,000,000
X_2	70,000,000
X_3	40,000,000
Y	70,000,000
Z	10,000,000
Haulways and service areas	100,000,000
Total	500,000,000

This volume can be thought of as an 18-foot deep pit, one mile square. Additional space is available in the area of current mining and is being created at the approximate rate of 15,000,000 cubic feet per year.

The Storage Concept

Early in the study, the concepts of retrievable versus non-retrievable storage were debated. It was decided that, for this study, underground waste emplacement should be based on long-term secured storage which makes for more efficient utilization of the mine space. Retrieving the long-term stored waste would be considered only in an emergency and when no other alternative was available. However, in order to develop cost data associated with short-term storage of the waste and its retrieval, cases were included in which a portion of the waste is stored temporarily and later retrieved, i.e., brought back to the surface and shipped.

General Criteria Considered: A number of general criteria were considered in formulating the storage concept. This includes:

- Waste storage will be long-term storage without planned retrieval of stored

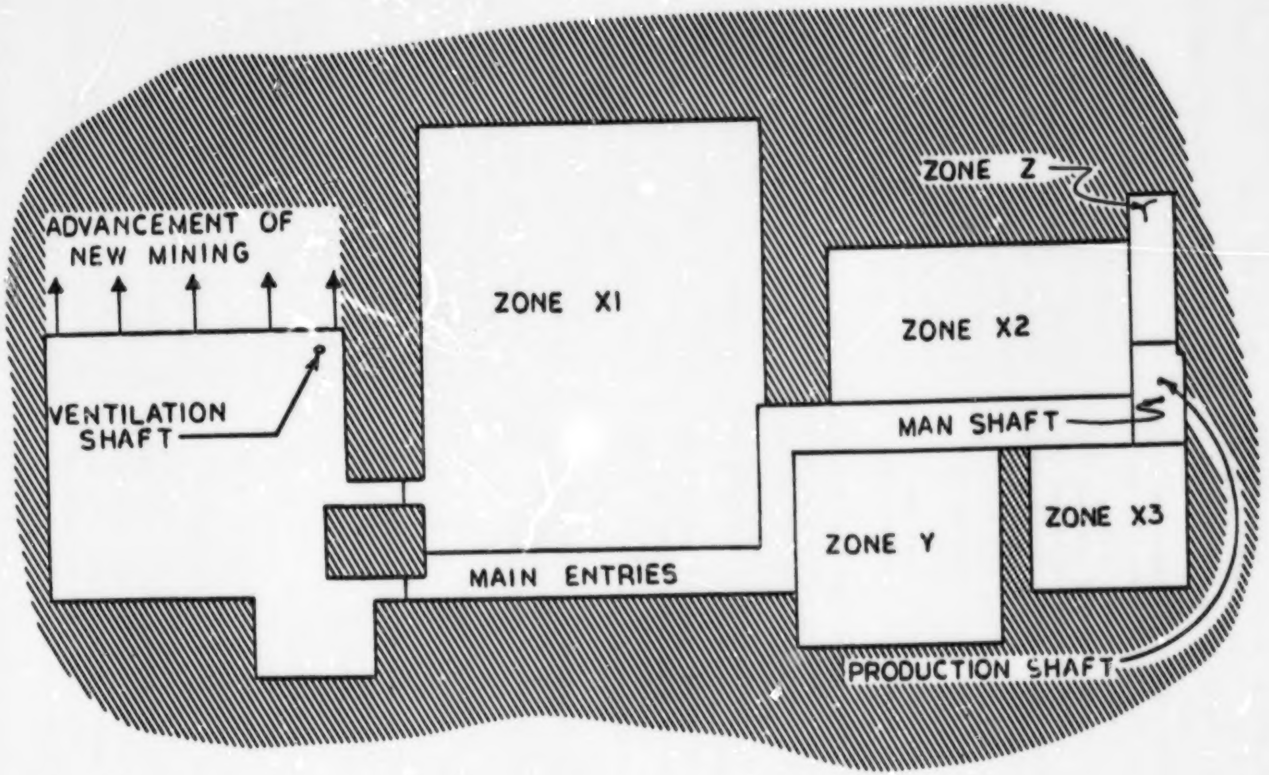
ADVANCEMENT OF
NEW MINING
VENTILATION
SHAFT
ZONE X1
MAIN ENTRIES
ZONE Z
ZONE X2
MAN SHAFT
ZONE Y
ZONE X3
PRODUCTION SHAFT

Fig. 3 General mine layout

waste except certain types of waste that may be stored temporarily.

- Retrieval of the long-term stored waste will be considered only when an extreme emergency occurs.
- All wastes brought to the plant will be converted to the most stable chemical and physical forms using the best practical technology.
- Any substance that could generate toxic fumes, fire, hazardous vapor, or explosive material will be excluded.
- The storage operation will include all activities from waste receiving at the gate to waste emplacement in underground storage cells.
- All wastes brought to the plant will be stored, except the clean condensate from the filtrate evaporation.
- There will be no effluent from the plant, except sanitary wastewater and clean runoffs.
- The selected storage method will provide long-term environmental protection without perpetual maintenance of the stored materials.
- The selected storage method will use the available space effectively.
- The stored material will be inventoried to identify the waste type, quantity, and storage location, in case retrieval becomes necessary.

These criteria dictate that hazardous wastes brought to the plant have to be treated to precipitate any dissolved hazardous constituents and then dewatered. In addition, if the waste contains a component that may generate toxic fumes, the waste must be treated to remove or destroy the component. Cyanide, for example, must undergo chloride oxidation followed by lime precipitation and filtration.

The criteria also dictate that the waste has to be stored in a systematic manner to allow controlled handling, segregated storage of different wastes, short-term maintenance of stored waste, inventorying of the stored waste, and long-term protection of the environment. To meet these criteria, it was decided to containerize the wastes in open-top, 16-gauge, epoxy-lined 55-gallon steel drums. The waste storage system and overall operation are summarized in Figure 4.

In summary, the waste received at the storage plant will be treated to convert hazardous elements into relatively insoluble forms, then filtered to remove free water, and finally containerized in 55-gallon steel drums. The waste in steel drums will then be hoisted into the mine on pallets, each containing four drums. The pallets will be transferred to the storage cell where they will be stacked.

THE BASE PLANT CAPACITY AND ALTERNATIVE CASES

A hazardous waste plant of 1,250 tons per day (TPD) capacity (as received) was selected as the base case (Case 1) for this study. This represents approximately 685 TPD of hazardous waste stored in the underground mine after precipitation and dewatering. The 685 TPD capacity selected for the base case represents the capacity of the existing hoisting system during normal two-shift operation of the selected salt mine facility.

To evaluate the sensitivity of plant capacities on the design of the storage facility and the costs, two additional plant capacities -- one higher and one lower than the base case -- were also included in the study. The high-capacity case (Case 2) receives 1,875 TPD of hazardous wastes and stores 1,030 TPD, while the lower capacity case (Case 3) receives 188 TPD and stores 103 TPD. The proportions of the Type A, B, C, and D wastes in Case 2 and Case 3 are the same as that of the base case.

The 1,030 TPD storage (Case 2) represents an upper limit based on three-shift operation of the existing hoisting system operated at 75 percent of the design capacity. The 103 TPD storage (Case 3) represents a low capacity of one-shift operation of all underground facilities.

During the course of this study, it became apparent that Type A waste requires a complicated and extensive chemical treatment facility. To evaluate the concept of receiving only non-liquid (residue) types of hazardous wastes, a special case (Case 4) where only Types B and C wastes are handled is included in this study. Operation of Case 4 will be the same as that of the base case, except that it would require no chemical treatment and thereby reduces the surface activity considerably.

It also became apparent that the container cost will be a major item of the overall operating cost, and any storage method that eliminates the need of containerization would be very attractive.

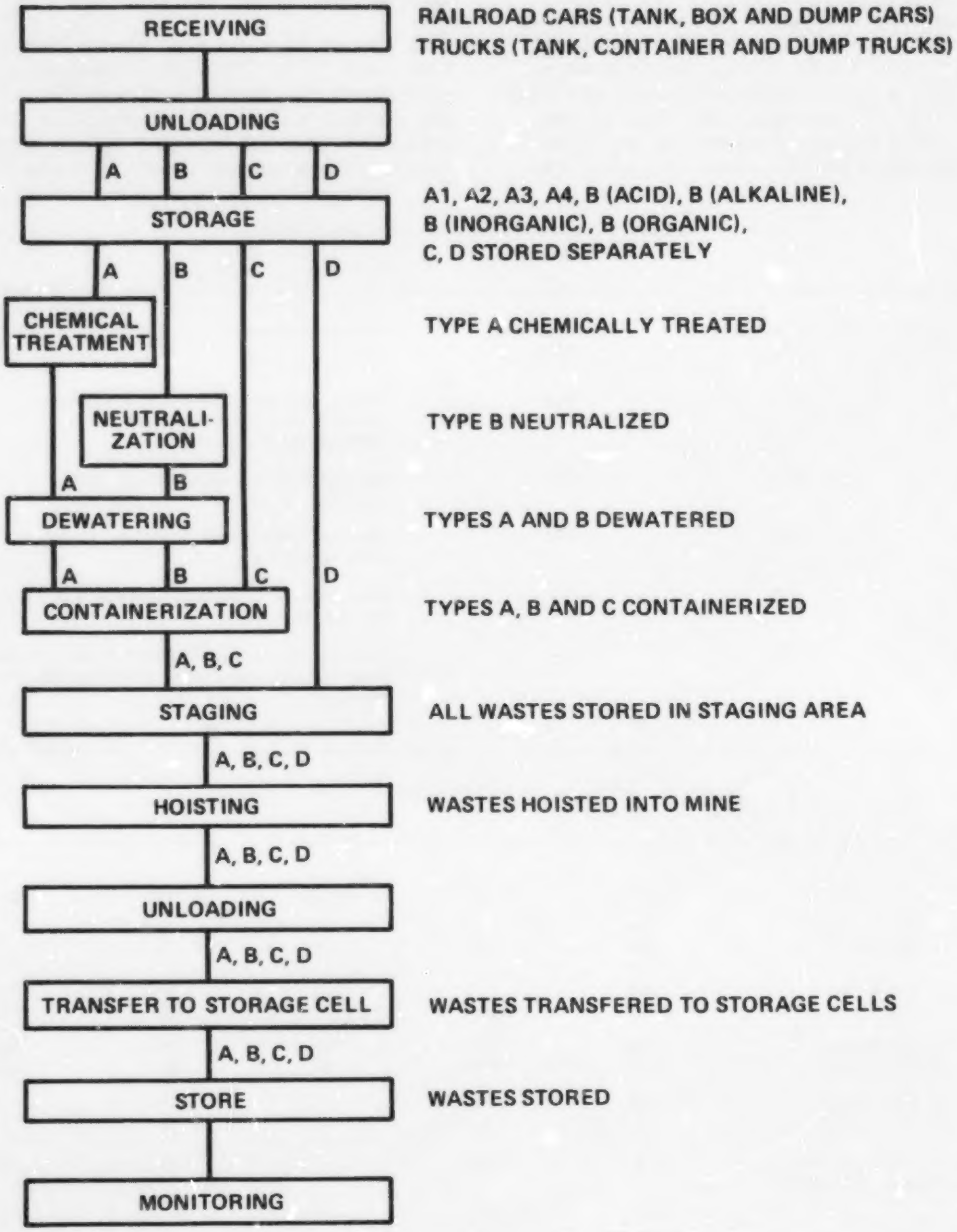
RECEIVING
RAILROAD CARS (TANK, BOX AND DUMP CARS)
TRUCKS (TANK, CONTAINER AND DUMP TRUCKS)
UNLOADING
A
B
C
D
STORAGE
A1, A2, A3, A4, B (ACID), B (ALKALINE),
B (INORGANIC), B (ORGANIC),
C, D STORED SEPARATELY
A
B
C
D
CHEMICAL TREATMENT
TYPE A CHEMICALLY TREATED
NEUTRALI-ZATION
TYPE B NEUTRALIZED
A
B
DEWATERING
TYPES A AND B DEWATERED
A
B
C
D
CONTAINERIZATION
TYPES A, B AND C CONTAINERIZED
A, B, C
STAGING
ALL WASTES STORED IN STAGING AREA
A, B, C, D
HOISTING
WASTES HOISTED INTO MINE
A, B, C, D
UNLOADING
A, B, C, D
TRANSFER TO STORAGE CELL
WASTES TRANSFERED TO STORAGE CELLS
A, B, C, D
STORE
WASTES STORED
MONITORING

Fig. 4 Underground storage of hazardous wastes

To explore the possibility of eliminating containerization, several presently available waste stabilization methods (solidification) were reviewed and one of these stabilization methods (Case 5) is included in this study. In Case 5, the non-liquid wastes (Types B and C) will be dewatered, mixed with a stabilizing additive, and then pumped into the storage cell area in the mine. Tables 1 and 2 summarize the five cases in terms of the types of waste, the quantities of waste received and stored, and storage concepts.

SURFACE FACILITIES AND OPERATION

In the storage concept chosen for the base case (1250 TPD waste received), a major portion of the handling operations occur on the surface before the material is rendered acceptable for emplacement in the mine. A list of the material handling steps for

Table 1 Waste Quantity and Treatment Summary

	Waste Received TPD	Waste Stored TPD	Storage Concept
Case 1	1250	685	Type A treated, Types A & B filtered, Types A, B & C containerized, Types A, B, C & D stored.
Case 2	1875	1030	Same as Case 1, except total plant capacity.
Case 3	188	103	Same as Cases 1 and 2, except total plant capacity.
Case 4	600	420	Same as Case 1 except, Types A & D are not included.
Case 5	600	420	Same as Case 4 except waste is stabilized (cementized) and stored directly into mine space.

Table 2 Waste Type Breakdown of Alternative Cases

	Case 1	Case 2	Case 3	Case 4	Case 5
Type A, TPD Received	600	900	90	0	0
TPD Stored	150	225	22	0	0
Type B, TPD Received	400	600	60	400	400
TPD Stored	200	300	30	200	200
Type C, TPD Received	200	300	30	200	200
TPD Stored	200	300	30	200	200
Type D, TPD Received	50	75	8	0	
TPD Stored	50	75	8	0	
Solids From Wastewater Evaporation, TPD Stored	85*	130	13	20	20
Total Received	1250	1875	188	600	600
Total Stored	685	1030	103	420	420

*85 TPD wastewater solids include 65 TPD from Type A and 20 TPD from Type B wastes.

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each waste type and sub-type would require several pages. The intent is to give a brief picture of the surface operations. The plant surface process facilities are designed to receive the four types of waste and temporarily store, treat, containerize and transfer them to the staging area for lowering into the mine. A number of auxiliary operations are required to support the main processing functions, e.g., materials (drums and pallets), and chemicals handling, process steam generation, electric power distribution, wastewater treatment and oily waste incineration. Administrative and maintenance functions are also part of the surface operation.

Waste Receiving and Processing

Figure 5 illustrates in block diagram form the main processing steps for each waste type. All four types are shipped to the plant by rail and by truck. Type D wastes (retrievables) are shipped only in 55-gallon drums; the others are shipped both in bulk containers and in drums.

Six hundred tons of Type A waste are received per day. Bulk shipments are pumped into storage tanks designated for storage of the particular A Waste subtypes, (Chromate, cyanide, acid, alkaline and nonreactive). Drummed wastes are emptied into

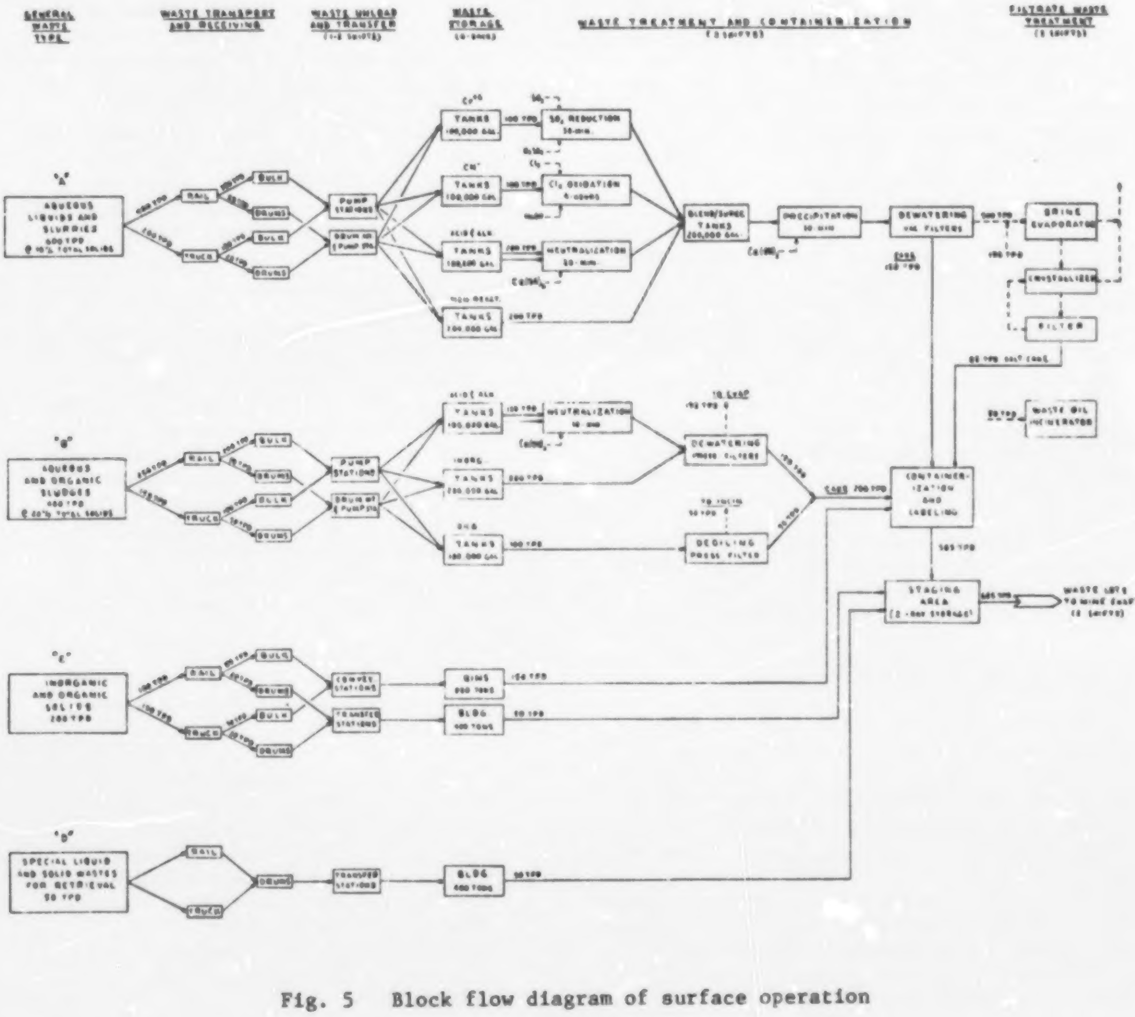
GENERAL WASTE TYPE
WASTE TRANSPORT AND RECEIVING
WASTE UNLOAD AND TRANSFER
WASTE STORAGE
WASTE TREATMENT AND CONTAINERIZATION
FILTRATE WASTE TREATMENT
"A"
AQUEOUS LIQUIDS AND SLURRIES 600 TPD
"B"
AQUEOUS AND ORGANIC SLUDGES 400 TPD
"C"
INORGANIC AND ORGANIC SOLIDS 200 TPD
"D"
SPECIAL LIQUID AND SOLID WASTES FOR RETRIEVAL 50 TPD
RAIL
TRUCK
BULK
DRUMS
PUMP STATIONS
CONVEY STATIONS
TRANSFER STATIONS
TANKS 100,000 GAL
BINS
BLDG
SO_2 REDUCTION
Cl_2 OXIDATION
NEUTRALIZATION
BLEND/SURGE TANKS 200,000 GAL
PRECIPITATION
DEWATERING
BRINE EVAPORATOR
CRYSTALLIZER
FILTER
WASTE OIL INCINERATOR
DEOILING PRESS FILTER
CONTAINERIZATION AND LABELING
STAGING AREA
WASTE LIFT TO MINE SHAFT

Fig. 5 Block flow diagram of surface operation

transfer tanks and pumped to the appropriate storage tanks. A nominal four-day storage capacity is provided for each waste subtype. Waste containing hexavalent chromium is reduced with sulfurdioxide to produce trivalent chromium. Cyanide bearing waste is oxidized with chlorine to nitrogen and CO_2. Acid and alkaline wastes are neutralized. Heavy metals are then precipitated as hydroxides by addition of lime. The precipitates are dewatered by vacuum filtration to a minimum 40 percent solids cake for waste containerization. One hundred fifty tons per day of filter cake are produced.

Four hundred tons of Type B waste are received per day. These are also pumped into storage tanks designated for the particular B Waste subtypes (acid, alkaline, neutral inorganic and organic sludges). Acid and alkaline wastes are neutralized. Inorganic and organic wastes are kept separate. All are dewatered or deoiled by automatic pressure filtration to a minimum 40 percent solids cake for waste containerization. One hundred fifty tons of inorganic filter cake and fifty tons of organic filter cake are produced each day. All waste receiving and processing is two shifts per day operation.

Two hundred tons of inorganic and organic Type C wastes are received per day. Bulk wastes are transferred to bulk storage bins. Wastes in 55-gallon drums are transferred to the drummed waste storage building. These solid wastes receive no treatment.

Fifty tons per day of Type D waste are received in 55-gallon drums. These wastes, designated for retrieval, are stored in a building and receive no treatment.

Containerization and Staging

Five hundred eighty five tons of waste are put in 55-gallon drums during two shifts of operation each day. About 2,000 drums and 500 wood pallets per day are used in the containerization facility. Six nearly-automatic containerization lines are operated, each in which empty drums on a conveyer system are filled, weighed, closed, labelled and palletized. Four-drum pallets are picked up by fork lift trucks and transferred to the staging area (building) near the production shaft.

In the staging building loaded pallets are stacked four-high in segregated pallet banks according to the emplacement designation of waste types, i.e., inorganic (X), organic (Y) and retrievable (Z). Only one of these three types is normally lowered into the mine during a shift. This permits shipment to only one emplacement area in the mine during a shift. The staging area is the interface between surface and subsurface operations.

Figure 6 schematically illustrates the basic surface processing steps through containerization and staging at the production shaft.

Effluent Waste Treatment

Aqueous filtrates and other plant wastewaters are processed in an evaporation-crystallization-filtration system which recovers 85 tons per day of contaminated salt cake which must be stored in the mine. Water is recovered as clean condensate for reuse and ultimate discharge (net water output). Oily filtrates are burned in a waste incinerator unit equipped with a two-stage scrubber for flue gas cleanup.

Surface Site Development

The layout of the surface civil structures and buildings is shown in Figure 7 for the base case plant. Of the total 17-acre fenced area, 15 acres are within the present mine boundary and two acres will have to be purchased from the local residents. Except for the production shaft, the main shaft and some portion of the railroad tracks, all surface structures will be new. About 13 acres of land will have to be cleared, including all of the existing buildings except the shaft houses.

The surface facilities include all of the mechanical equipment (piping, electrical, instrumentation) and the following new civil structures and buildings:

- Truck scale office and pad
- Rail scale office and pad
- Tank truck unloading platform
- Dump truck unloading building
- Tank and hopper car unloading building
- Box car unloading platform
- Drum unloading platform
- Chemical unloading platform
- Chlorine unloading platform
- Storage tank area

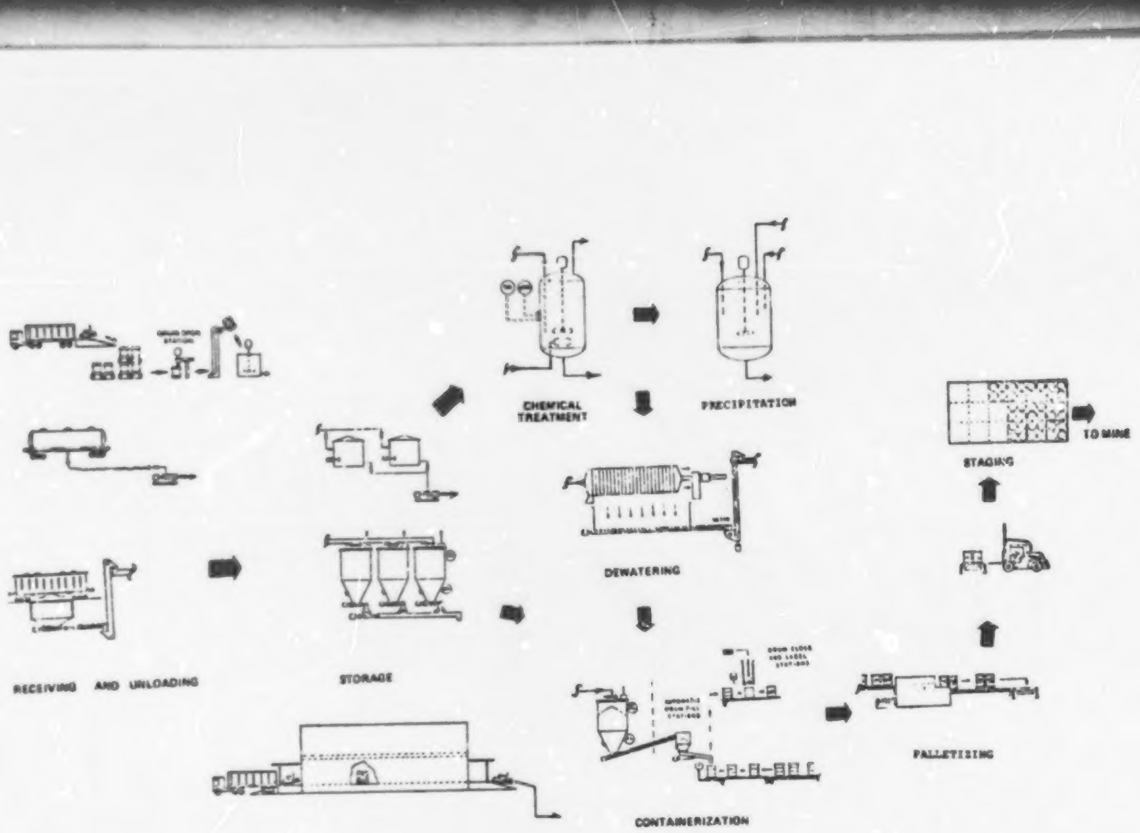

Fig. 6 Schematic diagram of surface operation

- Drum waste storage building
- Waste treatment building
- Filtration building
- Containerization building
- Staging building
- Administration building
- Safety/medical building
- Laboratory
- Equipment storage building
- Warehouse
- Shops
- Drum cleaning building
- Wastewater collection ponds
- Wastewater treatment and filtration building
- Boiler house

SUBSURFACE FACILITIES AND OPERATION

Major underground facilities include shafts, ventilation systems, underground staging area, haulways, storage cells and service buildings. The subsurface operation starts with the transfer of drummed wastes from the surface staging area to the production skip in the same building.

Waste Storage

Subsurface operations are depicted in Figure 8 and include:

- Surface loading and lowering into the mine
- Underground unloading and staging
- Hauling to storage zones
- Storage
- Storage cell preparation
- Monitoring
- Record keeping.

At the surface, a fork lift truck places four pallets (16 drums) on the skip and a utilityman secures the load. Upon a "ready" signal, the loaded skip is lowered 1,400 feet into the mine. A lowering cycle takes five to seven minutes - 1 1/2 minutes of actual lowering time.

At the base of the shaft, a forklift takes the four pallets out of the skip and sets them aside. Another forklift picks up two pallets at a time and loads them onto a waiting flat bed haul truck. A staging area near the shaft has one-day's waste storage capacity and can be used if there is any reason to stop direct haulage to the storage cells.

Tractor-trailers haul 20-pallet loads (25 tons) from the shaft area to the storage zones. Round-trip distances to the X, Y, Z storage zones (see Figure 3) vary from

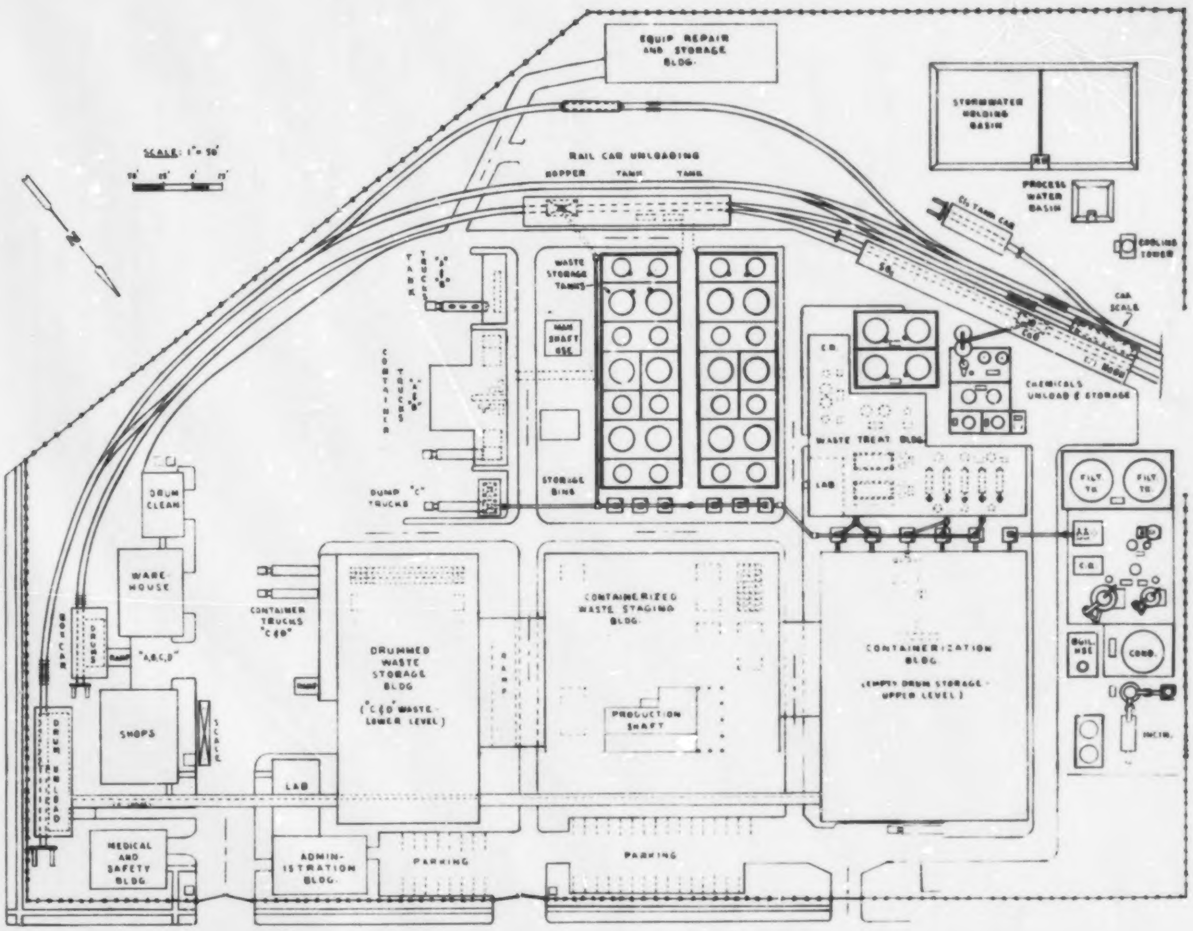
SCALE: 1" = 50'
50' 25' 0' 25'
N
EQUIP REPAIR AND STORAGE BLDG.
STORMWATER HOLDING BASIN
PROCESS WATER BASIN
COOLING TOWER
RAIL CAR UNLOADING
HOPPER
TANK
TANK
Cl2 TANK CAR
SO2
CAR SCALE
C&D
Cl BLDG
CHEMICALS UNLOAD & STORAGE
TANK TRUCKS
CONTAINER TRUCKS "A&B"
WASTE STORAGE TANKS
MAN SHAFT USE
STORAGE BINS
DUMP "C" TRUCKS
C.R.
WASTE TREAT BLDG.
LAB
FILT. TK.
FILT. TK.
C.R.
BOIL. HSE
COND.
INCIN.
DRUM CLEAN
WARE-HOUSE
BOX CAR
DRUM
"A,B,C,D"
RAMP
SHOPS
SCALE
DRUM UNLOAD
CONTAINER TRUCKS "C&D"
DRUMMED WASTE STORAGE BLDG
("C&D" WASTE-LOWER LEVEL)
CONTAINERIZED WASTE STAGING BLDG.
PRODUCTION SHAFT
CONTAINERIZATION BLDG
(EMPTY DRUM STORAGE-UPPER LEVEL)
LAB
MEDICAL AND SAFETY BLDG
ADMIN-ISTRATION BLDG.
PARKING
PARKING

Fig. 7 Plot plan of surface facilities

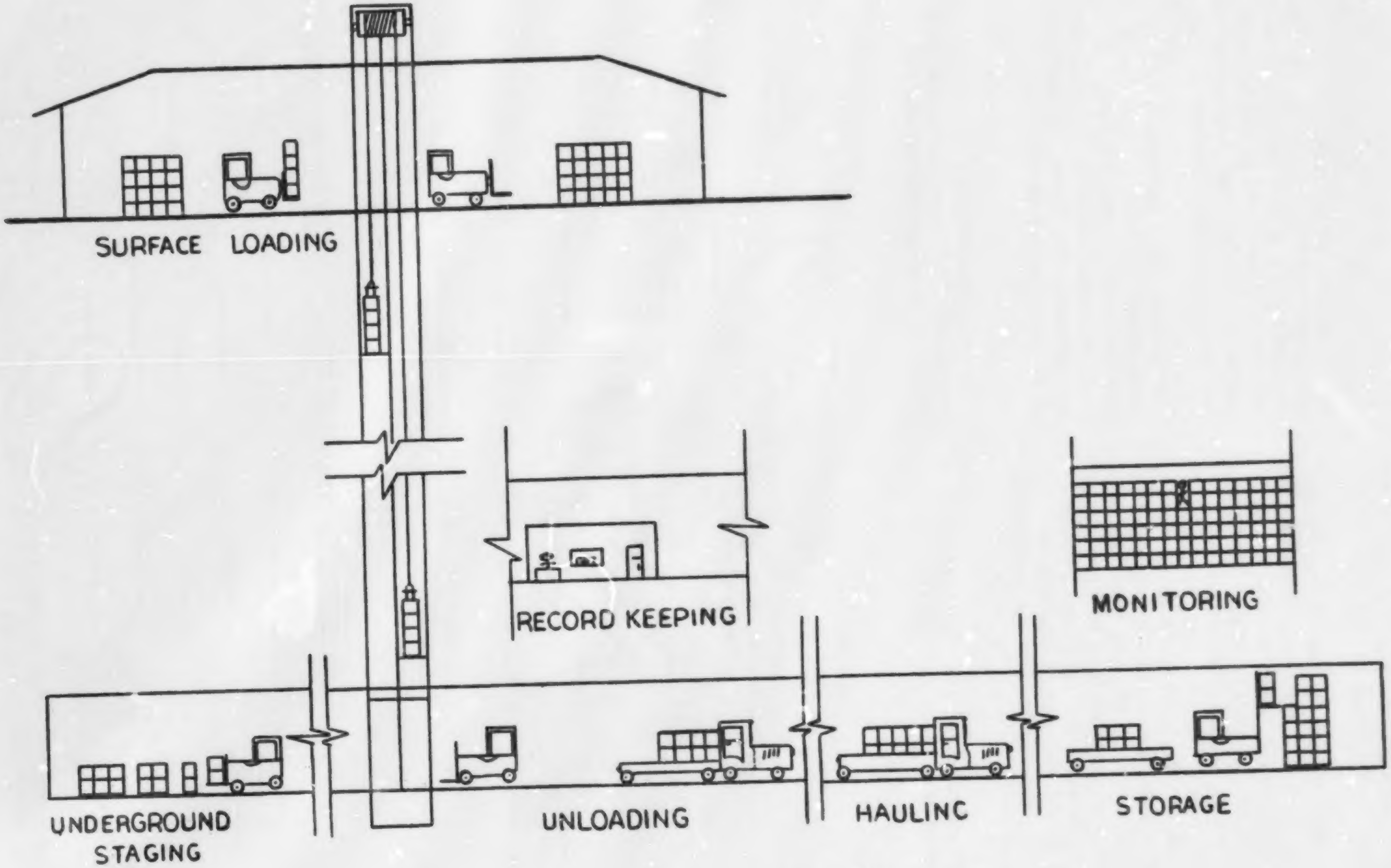
SURFACE LOADING
RECORD KEEPING
MONITORING
UNDERGROUND STAGING
UNLOADING
HAULING
STORAGE

Fig. 8 Schematic diagram of subsurface operation

a 3,000 foot average to Zone Z to an 18,000 foot average to sections of Zone X.

Storage takes place in any of five zones: X_1, X_2, X_3, Y, Z). Each zone is formed by many interconnecting rooms (cells) about 60 ft. by 60 ft. by 20 ft. high. Unmined salt barriers or ventilation stoppings isolate the zones. In the long term storage zones (X and Y), forklifts unload two pallets at a time and stack them six pallets high in the cell (Figure 9). The pallets are locked together for additional stability. An average "full" cell would hold about 1,200 pallets, including an allowance for side clearance and monitoring access.

Figure 10 illustrates the short-term storage operation - Zone Z. The storage density is much lower in order to maintain ease of retrieval. After an initial two-year buildup of material (24,000 pallets), the amount of waste sent to storage is assumed to be offset by a similar amount retrieved from storage and hoisted to the surface. Storage and retrieval operations are conducted concurrently.

A storage cell preparation is a major underground activity. Preparation involves removing waste salt and debris, scaling the roof and ribs, bolting the roof and grading and brushing the floor. A one-month supply of prepared rooms is maintained.

Waste monitoring and recordkeeping, although not discussed here, are also very important underground activities.

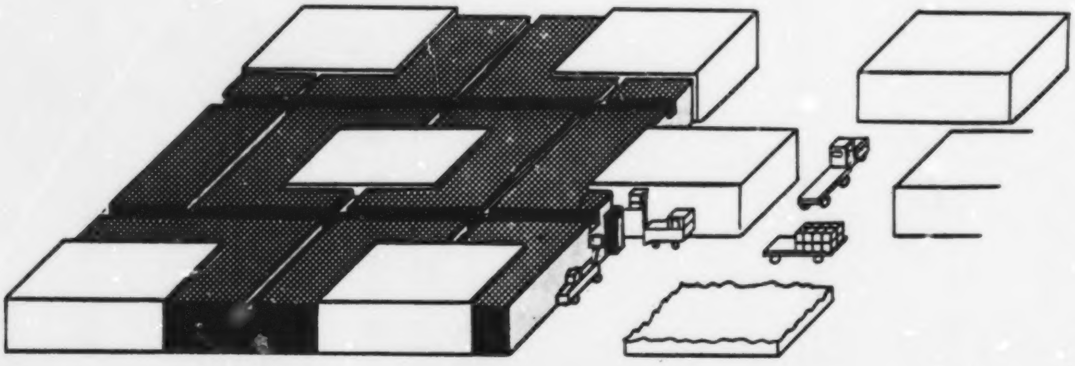

Fig. 9 Schematic diagram of long-term storage operation

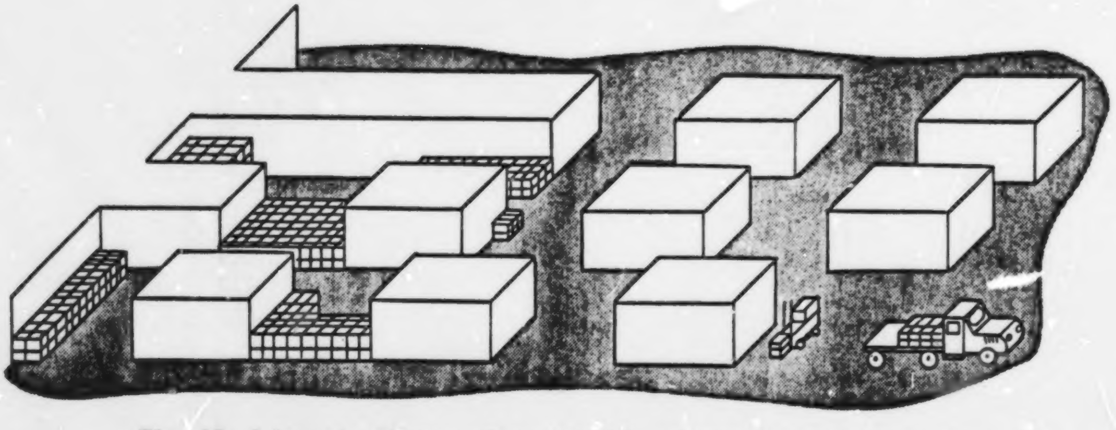

Fig. 10 Schematic diagram of retrievable storage (Type D) operation

New Underground Facilities

Mine rehabilitation, installation of a ventilation system and new underground service buildings comprise the bulk of the civil/structural works. New subsurface equipment are largely mobile equipment for material hauling.

Non-Container Storage Case

In Cases 1 through 4, all wastes are stored in drums. To eliminate containerization, the waste stabilization method (Case 5) is considered.

As in Case 4, only Type B and C wastes are received in Case 5. The wastes are neutralized, dewatered, and mixed with a cementizing agent before being pumped into the mine. In the mine, the wet mixture is pumped into a prepared cell where it is cured to form a solid mass. The concept of the waste stabilization and direct storage into the mine is shown in Figure 11.

ECONOMIC EVALUATION

The capital costs (first quarter 1977 dollars) were estimated based on lists and specifications of equipment, buildings, civil structures, and mine rehabilitations. The capital costs include the following items:

- Existing mine facilities
- Site development
- Buildings, civil structures, and mine rehabilitation
- Equipment, piping, electrical, and instrumentation
- Engineering service, allowance during construction and contingency.

Table 3 summarizes the capital cost for Cases 1, 4 and 5.

Table 3 Capital Cost Summary

Item	Base Case Case 1	Case 4	Case 5
	$1000's	$1000's	$1000's
WASTE QUANTITY			
Received Waste, Tons/Yr	375,000	180,000	180,000
Stored Waste, Tons/Yr	205,500	125,000	126,000
EXISTING MINE	30,000	30,000	30,000
NEW SURFACE FACILITY, DIR. FIELD COST	28,013	15,101	12,311
NEW SUBSURFACE FACILITY, DIR. FIELD COST	8,229	8,197	8,060
TOTAL INDIRECT FIELD COST @ 6% of TDFC	2,175	1,398	1,222
ALLOWANCE DURING CONSTRUCTION & ENG. SERVICE @ 1% of TFC + $500,000 + 15% of TFC	6,647	4,151	3,955
CONTINGENCY @ 25% of TFC	9,604	6,174	5,398
TOTAL CONSTRUCTION COST	54,668	35,321	30,946
WORKING CAPITAL	5,467	3,532	3,095
TOTAL INVESTMENT	90,135	68,853	64,041

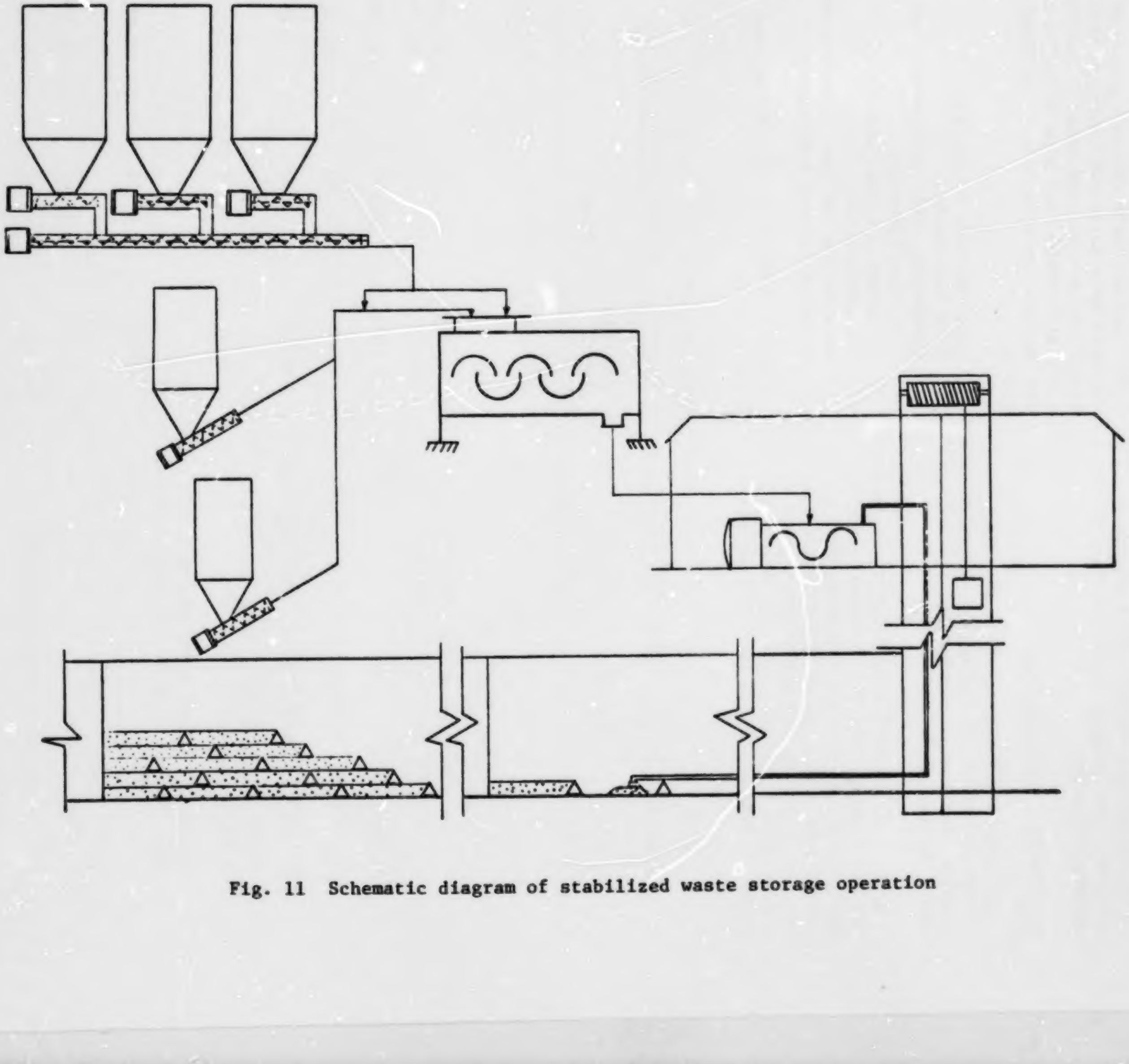

Fig. 11 Schematic diagram of stabilized waste storage operation

The operating costs (first quarter 1977 dollars) were estimated from conceptual operating plans, including a list of manpower requirements and an estimation of material requirements. The operating costs include the costs of:

- Direct material and labor
- Maintenance material and labor
- Overhead material and labor
- Taxes and insurance, depreciation, and long-term liability insurance

Table 4 summarizes the operating cost of Cases 1, 4, and 5.

Cases 4 and 5 eliminate the liquid waste (Type A) and the retrievable waste (Type D) handling. This is reflected in the much lower costs of the surface facilities.

Table 4 Operating Cost Summary

Item	Base Case Case 1	Case 4	Case 5
	$1000's	$1000's	$1000's
WASTE QUANTITY			
Received Waste, Tons/Yr	375,000	180,000	180,000
Stored Waste, Tons/Yr	205,500	126,000	126,000
TOTAL CAPITAL COST	90,135	68,853	64,041
DIRECT OPERATING COST			
RAW MATERIALS & UTILITIES	16,828	9,203	1,048
DIRECT LABOR			
Operating Labor	3,695	2,533	1,658
MAINTENANCE, LAB & MAT.	5,208	3,400	2,635
INDIRECT OPERATING COST			
ADMINISTRATION & GENERAL OVERHEAD	1,823	1,273	900
TAXES AND INSURANCE			
@ 2% of Plant Cost and $1.10 per ton for Long Term Liability Insurance	2,215	1,575	1,479
OPERATING COST	29,769	17,984	7,720
$/Ton Received	79	100	43
$/Ton Stored	145	143	61

Operating cost (excluding cost of capital and depreciation) is about $30 million per year for the base case, of which 45 percent is the cost of 55-gallon drums and pallets. The cost of containers (drums and pallets) alone is $65 per ton of waste stored in the mine ($35.70 per ton received). There is a substantial economic incentive to look at alternative storage concepts that do not involve containerization.

Case 5, which eliminates the use of containers, reflects a considerably lower operating cost in terms of dollars per ton stored.

Unit Cost Per Ton

To get a comparison of the economics, the unit cost per ton (total cost per ton including return on investment) was estimated for all five alternatives based on the discounted cash flow net present value methodology. The unit costs were computed for private and government ownerships. The private ownership is based on a 10 percent return on investment, 100 percent equity, and 48 percent income tax, while the government ownership is based on a 100 percent financing at 6 percent cost of capital and no income tax. Results are summarized in Tables 5 and 6.

Plant capacity has the expected effect on the unit cost. As can be seen in Figure 12, the unit cost drops by about 50 percent as the plant capacity increases from about 50,000 to about 250,000 tons processed (received) per year. Thereafter, the effect on the unit cost is lessened.

Table 5 Waste Management Fee of Alternative Plant Sizes

Item	Base Case 1	Case 2	Case 3
Waste Quantity			
Received, tons/yr	375,000	562,500	56,250
Stored, tons/yr	205,000	309,000	30,900
Total Capital ($1,000)	90,135	104,075	61,494
Economic Life (Years)	30	20	40
Waste Management Fee			
Private Ownership[1]			
$/ton of Received Waste	131	117	377
$/ton of Stored Waste	240	213	686
Government Ownership[2]			
$/ton of Received Waste	101	95	233
$/ton of Stored Waste	185	173	424

Note: (1) Private ownership assumed 10% return on investment.

(2) Government ownership assumed 6% cost of capital.

Table 6 Waste Management Fee of Alternative Storage Methods

Item	Adjusted Case 1	Case 4	Case 5
Waste Quantity			
Received, tons/yr	229,300	180,000	180,000
Stored, tons/yr	126,000	126,000	126,000
Total Capital ($1000)	--	68,853	64,041
Economic Life (Years)	--	40	40
Waste Management Fee			
Private Ownership			
$/ton of Received Waste	210*	179	118
$/ton of Stored Waste	382*	257	168
Government Ownership			
$/ton of Received Waste	164*	131	71
$/ton of Stored Waste	298*	187	102

*Adjusted to reflect the cost at 126,000 tons per year.

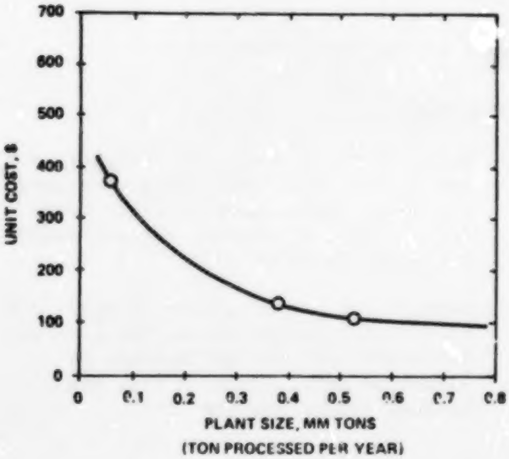

Fig. 12 Sensitivity of unit cost to plant size

The sensitivity of unit cost to the cost of the mine is shown in Figure 13 for a mine cost up to $100 million. A $70 million increase in the mine cost would add about $40 per ton to the $131 base case unit cost in this example.

Table 6 shows the unit costs of Cases 4 and 5 and compares them with the base case costs. Cases 4 and 5 process the same two types of wastes (Types B and C), but Case 4 would containerize the waste, while Case 5 would stabilize the waste to eliminate the containers. To compare the unit costs of these different storage concepts based on the same underground storage loading, the base case unit cost was adjusted to reflect the cost at 126,000 tons per year (420 tons per day). In the case of government ownership, the Case 4 unit cost (187 per ton stored) is almost twice of the Case 5 unit cost ($102 per ton stored). The Case 1 unit cost ($298 per ton stored) is almost three times the Case 5 unit cost.

The numbers seem to say it will cost a lot to store hazardous wastes in a salt mine. The cost can be reduced somewhat by minimizing the needed surface treatment facilities (though the waste generators would incur additional costs for converting

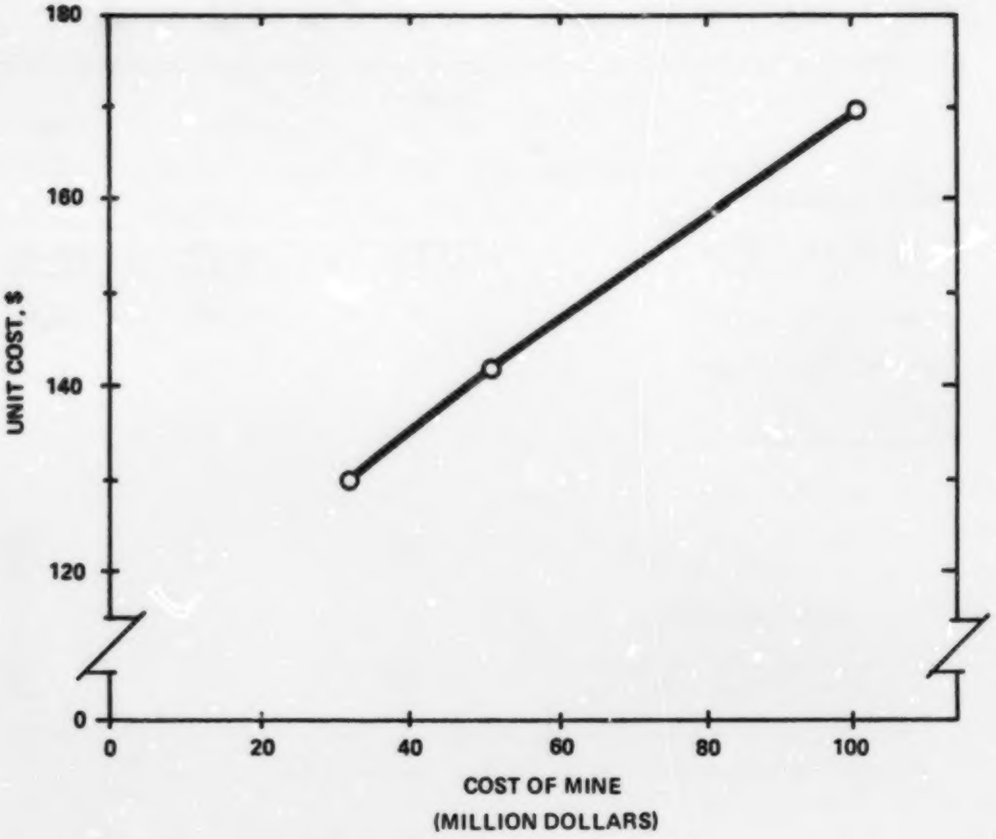

Fig. 13 Sensitivity of unit cost to the cost of mine

these wastes into a form acceptable for emplacement). The cost may be reduced by using a direct storage concept that eliminates expensive containers.

There is one important point. The study mine can only store a small portion of hazardous waste generated in this country. Underground mines suitable for storing hazardous waste is limited. Mine space is a valuable resource and should not be misused by storing wastes that could be readily disposed by other means.

REFERENCES

1. Stone, R.B., Aamodt, P.L., Engler, M.R., and Madden, P., "Evaluation of Hazardous Waste Emplacement in Mined Openings," Fenix & Scisson, Inc., EPA-600/2-75-040, December 1975.

2. Kown, B.T., Stenzel, R.A., Hepper, J.A., Ruby, J.D., and Milligan, R.T., "Cost Assessment for the Emplacement of Hazardous Materials in a Salt Mine," Bechtel Corp., November 1977.

ASSESSMENT OF DEEP WELL INJECTION OF HAZARDOUS WASTE

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ABSTRACT

In response to specific requirements to assess technologies available for managing hazardous waste, a review and analysis was completed on available information related to the injection of hazardous waste into deep wells. Based upon this information, assessments were made as to the adequacy of this method for managing hazardous wastes and ensuring proper environmental protection. Additional work provided detailed information on the application of the technology.

The analysis indicated that geologic and engineering data available for many areas are sufficient to properly locate, design, and operate a deep-well injection system. Serious problems, however, have been encountered because of failure to properly use the data and proven engineering techniques. Information available on saline aquifer chemistry, and the chemical and microbiological reactions within the receiving saline aquifer was judged inadequate in many areas.

This paper will summarize the large amount of information generated during these studies.

INTRODUCTION

The primary objective of this symposium is to provide up-to-date information on research being conducted by the Solid and Hazardous Waste Research Division (SHWRD), particularly in the area of disposal/management of hazardous wastes via the land. This presentation deals more with data gathering and assessment of available information on deep-wells than with research. However, the deep-well injection of industrial and/or hazardous waste is of interest as a technology for managing liquid hazardous wastes, and thus a discussion of SHWRD deep-well activities is appropriate.

In 1974, in anticipation of new legislative requirements in hazardous waste management, the U.S. Environmental Protection Agency's (USEPA) Office of Solid Waste (OSW) initiated programs to assess technologies available or nearly available for managing hazardous wastes.[1] Subsurface injection of these wastes into deep wells was considered. The OSW therefore requested the Office of Research and Development (ORD), SHWRD, to conduct an assessment of deep-well injection as an environmentally sound technology for managing and controlling liquid hazardous wastes. The agency has completed inventories of injected wells under various contracts.[2] But the OSW had specific needs not addressed by these inventories. One basic need was to have available information on deep wells assembled in one place. The important need, however, was to make an assessment of the environmental consequences of injecting hazardous wastes into appropriate subsurface formations. An impossible task! Many have expressed real concern over the impossibility of determining the final disposition of the waste after injection. They also expressed concern that no one can guarantee that eventual severe environmental problems will not result. Others state that the technology is completely acceptable.

Notwithstanding, SHWRD issued a request for proposals to conduct the assessment. The contract period of only 4 months was dictated by the timetable established for OSW outputs. Some additional outputs required dealing with well design, and operation guidelines followed the assessment task. It is important to note that the assessment and the follow-up work were based solely on available information--no laboratory or field investigations were performed.

This paper summarizes two studies supported by SHWRD. First, the comprehensive review, data gathering, and assessment study conducted by Louis R. Reeder, et. al.,[3] and second, a follow-up report by Warner and Lehr[4] on the technology and best available practices for proper implementation of wastewater injection into deep wells.

Considerable interest has been shown in the assessment results, and some controversy has arisen. The follow-up work, which will appear in the second report, has not yet been published, so the discussion here will focus on the assessment findings, conclusions, and recommendations.

STATUS OF DEEP-WELL INJECTION

Briefly, deep-well (subsurface) injection normally refers to the injection of liquid waste into selected rock formations that are below and isolated from fresh water aquifers. The prefix "deep" does not refer to any specific depth. The concept of underground injection of liquid waste was probably started by the oil industry when they began to inject waste salt brines back into the subsurface reservoirs from which the oil and salt brines were produced. The first controlled use of deep-well injection for disposal of industrial waste is difficult to determine. A look at the growth figures (Figure 1) and the inventories conducted through the years does, however, provide some information on the historical aspect of deep-well injection. These inventories show only four such wells constructed before 1950, whereas the most recent inventory (1975) listed 322 industrial and municipal injection wells, of which 209 were operating.[4] The following list shows their distribution across the country:

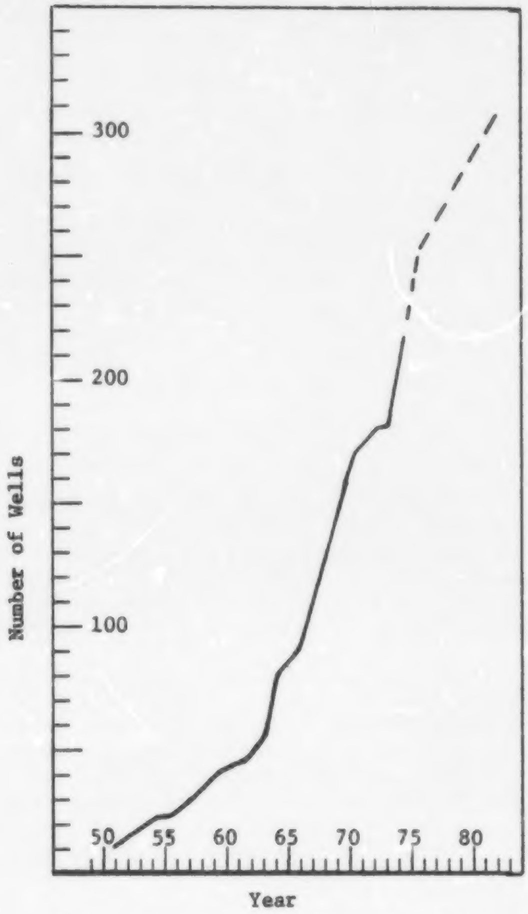

Figure 1. Growth of Operating Deep-Well Injection Systems in the United States.

Texas	91
Louisiana	65
Kansas	30
Oklahoma	15
Industrialized North and East Central States	73
Other States	48

TECHNOLOGY ASSESSMENT

A governing principle of deep-well injection of industrial waste is to dispose of a maximum amount of hard-to-treat, toxic, hazardous, or innocuous waste at a minimum cost, with the least deleterious effects on the environment. The term "least" may be applied to an effect such as odor, which is of relative importance. Assurance that the environmental effects are acceptable is perhaps the major uncertainty facing the technology.

In the Reeder study,[3] the contractor's primary task was to make an assessment of the capability of the technology to protect the environment by compiling and analyzing existing data. The waste of concern for this effort was defined as any industrial toxic or hazardous waste. The contractor was directed not to consider oil field brines, similar brines, or wastewaters unless they were determined to present special problems. Because the major work was to be completed in only 4 months, the study took the following form.

REVIEW

This task usually appears in the contract scope-of-work. In this case, however, it had tremendous significance to the ultimate output. Since no field or laboratory investigations were to be done, the important assessment had to be based on available information. The review included many discussions with experts involved with deep-well activities, detailed review of available literature, and discussions with regulatory officials, State and Federal goverments, and university and other research organizations.

ENVIRONMENTAL AND TECHNOLOGY ASSESSMENT

Based on the reams of information gathered through the review task, the contractor assessed the ability of a deep-well injection system to accept and manage hazardous waste in a manner that would insure protection of the environment. The contractor was directed to give precedence to environmental aspects over all other considerations.

Additional details of the assessment are useful in providing insight as to the nature of this task. The contractor was directed to review and technically evaluate such factors as:

--Detection, monitoring, and control technology available or being developed to monitor and control the waste injection operation and system. (Detection of and monitoring of faulty operations, breaks, leakage, and similar problems were considered.)

--Potential for the injected waste to migrate or be transported from the receiving reservoir into areas where potentially harmful environmental effects could result.

--Geological criteria used to select well sites.

--Well engineering design, installation, and operating requirements.

--Waste characterization, pretreatment, and handling requirements. (This included the chemical, biological, and physical properties of the waste. Potential interactions between the wastes and the receiving formations were considered.)

The review and the assessment tasks were the most critical ones, but others were also extremely important in providing needed input to the assessment task and in fulfilling OSW needs. Other tasks included representative case studies depicting examples of good and bad deep-well injection practices, compilation and characterization of hazardous wastes being injected, assessment of regulatory programs and controlling statutes, compilation of ongoing research projects, and recommendations for required research and/ or demonstration activities.

TECHNOLOGY APPLICATION GUIDE

As a follow-up to the assessment study, the Robert S. Kerr Laboratory, with support from the Municipal Environmental Research Laboratory (MERL), implemented and compiled a report on acceptable practices for deep-well injection. The effort developed information on injection well construction and maintenance that can be used as a guide and standard for those involved in planning, design, construction, operation, and abandonment of injection wells. The report was developed in conjunction with the National Water Well Association.

ASSESSMENT STUDY FINDINGS

A clear presentation and discussion of findings from the assessment study are difficult. The assessment was completed based on available data and some subjective factors. Add to this the judgment calls required by the investigators to determine alternatives in completing the work, and one realizes the potential pitfalls in making a scientific assessment. Nevertheless, large amounts of useful data were generated, and some important conclusions were reached by the study. The following is a summary of the findings for the assessment study. Discussion is arranged according to the categories presented in the final report. The reader is cautioned again to note the waste of concern for the study.

GEOLOGICAL CONSIDERATIONS

Geological information available is judged adequate to divide the United States into the following areas:

- --Areas in which deep-well injection is feasible and may be performed safely.
- --Areas where injection is possible but may produce detrimental effects to the environment.
- --Areas where injection is either impossible, marginal, or will definitely have detrimental environmental effects.

Information presented classifies broad geomorphic areas in the United States as to apparent geologic compatibility with deep-well injection. In most cases, the information identifies areas feasible for safe injection. Detailed geological investigations must still be made, however, for any given well site within an area rated as acceptable. Ten criteria are provided for determining the feasibility of a well site within an acceptable area. These are:

- --Uniformity
- --Large areal extent
- --Substantial thickness
- --High porosity and permeability
- --Low pressure
- --A saline aquifer
- --Separation from fresh water horizons
- --Adequate overlaying and underlaying aquicludes
- --No poorly plugged wells nearby
- --Compatibility between the mineralogy and fluids of the reservoir and the injected waste.

A reservoir properly selected will be able to safely contain wastes injected into it, provided the injected volume does not exceed the available volume of the reservoir and injection pressures do not exceed critical formation pressures. There is an important caveat: these criteria for reservoir selection do not take into account possible destruction of the reservoir integrity by improper operations or by forces of nature such as earthquakes.

ENGINEERING CONSIDERATIONS

Basically, engineering for well design and construction is judged available and adequate to safely handle wastes being injected. The design of any given system must be based on consideration of the effects of all factors related to the reservoir, the wastes, and the physical dimensions of the well. In addition, operating limitations must be established for every well to ensure that the limits of the equipment, the reservoir, and the confining beds are not exceeded. Such excesses could release the waste from the well bore or the saline aquifer.

CHEMICAL CONSIDERATIONS

If we assume proper well design and operation, the success of injecting less hazardous or relatively innocuous chemicals into deep wells depends on the formation, the fluids in the formation, and the other chemicals in the waste streams.

Because waste streams are a mixture of different chemicals, their activity will be affected by all the chemicals in the stream. If acidic waste is not neutralized before injection or injected into a zone containing sufficient carbonate to dissipate the acid, it may be transported out of the injection zone and into a zone containing usable mineral resources, unless the host zone is sealed above and below by beds impervious to acid. Other chemicals may react to form plugging materials that will damage the formation and prevent migration of waste away from the well bore. Each waste stream should be evaluated to determine whether or not there is a better or safer method of disposal. If possible, some of the most hazardous chemicals and solids should be removed before injection if their removal and disposal can be done safely.

Hazardous materials with long persistence periods may cause unacceptable risks to the environment if disposed of in deep wells. The long storage periods required to reduce the chemical hazard to an acceptable level increases the risk that the waste will escape from the storage area because of system failure or because of migration of the fluids.

Long persistence and a very high human and ecological hazard rating make certain chemicals unacceptable for disposal in deep wells. Because these chemicals either do not degrade or have long persisence times, they pose a long-term potential hazard to underground water supplies. These chemicals include acrolein, arsenic and arsenic compounds, cadmium and cadmium compounds, carbon disulfide, cyanides, diazinon and other pesticides, fluorides, hydrocyannic acid, hydrofluoric acid, hexavalent chromium compounds, mercury and mercury compounds, and nitrophenol.

MONITORING

Although monitoring is judged as relatively effective in some operations of deep-well operations--especially in detecting equipment malfunction--an inherent weakness of available monitoring systems is that the detection of problems is usually after the fact. Monitoring wells may adequately detect waste passage within a reservoir, but it usually cannot confirm the escape of waste or vertical fluid movement.

CONTENTS OF THE FOUR-VOLUME REPORT

The four-volume report is divided as follows:

Volume I (215 pages) contains an executive summary and details on the geologic, engineering, chemical, microbiological, and other aspects important in the environmental and technological evaluations of injecting hazardous waste into deep wells. Narative detail is provided on waste characterization, well inventory, related case histories, research projects, economics of deep-well systems, legal considerations, and legislative and regulatory consideration. Also provided is a detailed glossary of terms.

Volume II (316 pages) contains Appendices A, B, and C. Appendix A is the Bibliography of literature used during the study. Appendix B is a compilation of patents related to deep-well systems. Appendix C provides available characterization profiles of chemical wastes being injected into deep wells.

Volume III (561 pages) contains Appendix D, which is the contractor's inventory of industrial waste injection wells through December 31, 1974. The inventory incorporates information gathered from previous inventories and supplemented by data collected from State agencies or individual operations. Location plates are included for the Texas and Louisiana wells, and the calculated radius of invasion is presented for wells where sufficient data were available.

Volume IV (413 pages) contains Appendices E, F, G, H, I, and J. Appendix E presents limited case histories of actual industrial waste injection well operations and provides examples of unacceptable and acceptable operations. Recent research on microbiological aspects of subsurface injection is discussed in Appendix F. Appendix G is a summary of research related to deep-well injection, and Appendix H is a summary of research dealing with treatment of hazardous wastes. Legislation, regulations, and policies governing deep-well injection operations are provided in Appendix I. As a result of EPA review of this document, there were a number of questions and issues raised as to the conclusions made versus those warranted based on available information. Appendix J was added by EPA to give readers the benefit of clarifying information that resulted from that review and from the contractor's response.

AN INTRODUCTION TO THE TECHNOLOGY OF SUBSURFACE WASTEWATER INJECTION

This report is in the publication process. As the title suggests, it deals with the technology and its proper application. From an environmental protection point of view, this report is an important addition to the available literature on deep wells. It was developed by the National Water Well Association, in conjunction with the EPA. In addition, to ensure that important views of the State and Federal governments and industry be reflected in the document, a panel of experts guided the development of the manual. These individuals were all expert in some facet of subsurface injection and helped to assure that the resulting document will stand the critical review of the profession. The planned use is as a guide and standard for those involved in the planning, design, construction, operation, and abandonment of injection well systems.

A most efficienct method of communicating what is contained in the report is to reproduce portions of the Abstract and Introduction to that report as follows:

> When wastewater is injected into deep wells for disposal it can pose a serious environmental threat unless the injection process is carefully planned and executed from start to finish.
>
> Local geologic and hydrologic conditions must be thoroughly investigated including such characteristics as structure, stratigraphy, composition and engineering properties of the underlying formations. The nature of injection and confining intervals will determine the conditions that the injection wells must meet, or whether such wells are even feasible. Specific information acquired through the use of cores, probes, and other tests, will help to pinpoint areas of potential difficulty, and should suggest ways to avoid these problems.
>
> Once an injection site has been selected, the injection interval must be tested to insure that it is physically, biologically, and chemically compatible with the wastewater to be injected. Both the injection interval and the wastewater must be examined to guarantee that each will remain stable over an extended period of time. If problems exist, the wastewater can be treated to make it more compatible with the injection interval. Failure to bring the wastewater and injection interval into compatibility can lead to excessive corrosion, clogging, well and plant damage, and may necessitate well abandonment.
>
> The injection well itself must be carefully designed and constructed to guarantee the safety and integrity of the injected wastewater as well as of the surrounding formations and nature resources. When construction of the injection well is completed, the well should undergo final testing to establish records of baseline conditions for future reference and comparison. At this time, operating procedures and emergency precautions should be established and approval should be obtained from the necessary regulatory agencies. Only then can full-scale wastewater injection begin.
>
> An operating injection well should be monitored throughout its working life for any changes in injection conditions that may lead to system failure. An injection well operator has the responsibility of knowing what and where the injected wastewater is, and for keeping adequate operating records. When an injection well system permanently ceases operating, the well must be properly sealed, and a record describing the method and date of sealing and the precise location of the well should be filed with the proper authorities. When the guidelines for injection well operation set forth here are followed, the safety and success of this method of wastewater disposal will be insured.
>
> ...
>
> *An Introduction to the Technology of Subsurface Wastewater Injection* has been prepared to assist engineers, geologists, and others in the tasks of planning, designing, constructing, operating, and regulating industrial and municipal wastewater injection well systems. It is apparent to anyone reviewing the literature that a great deal has been written about this subject in the past 25 and particularly the past 10 years. Also, there is an extensive literature base in the related fields of petroleum engineering and ground water hydrology that can be applied to injection well technology. One purpose of this publication is, therefore. to provide a summary of selected information in a form convenient for use by well operators, engineering consultants, and regulatory authorities in performing their respective tasks, so that injection wells may be used, where desirable, more efficiently and with a minimum potential for environmental damage.

Impetus for development of An Introduction to the Technology of Subsurface Wastewater Injection was provided by passage of Public Law 92-500, the Federal Water Pollution Control Act Amendments of 1972 and Public Law 93-523, the Safe Drinking Water Act of 1974. Both of these laws contain specific provisions concerning wastewater injection wells. Public Law 92-500 requires that in order to qualify for participation in the National Pollution Discharge Elimination System permitting program, states must have adequate authority to issue permits which control the disposal of pollutants into wells. Therefore, it is only technically necessary that a state have the authority to issue or deny permits to qualify. However, to do this it is necessary to have a program for permit evaluation. The Safe Drinking Water Act requires that EPA develop regulations for state underground injection control programs. The objective of the law is to insure that underground injection does not endanger drinking water sources. This guide is a technical document intended to complement the required EPA regulations.

Included in the technical guide are chapters concerning the units of measurement used in injection well engineering, the nature of the subsurface geologic and hydrologic environment, the means of acquiring subsurface geologic and hydrologic data, the criteria used for injection well site evaluation, the physical and chemical properties of wastewater, wastewater classification, pre-injection wastewater treatment, injection well design and construction, the procedures preparatory to injection, well operation and monitoring, and system abandonment. The flow of these chapters is approximately in the order that the material is used during the planning, constructing, operating, and abandonment of an injection system. References used in the text are listed and appendices included at the end of each individual chapter.

TO INJECT OR NOT?

A decision to use deep-well injection for disposal of hazardous wastes must depend on many factors. If one keeps in mind the nature of the waste under consideration during the assessment study, in conjunction with the overriding environmental considerations, there appear to be a number of statements in the report that contradict the basic conclusion that hazardous wastes can be safely injected. The following conclusion reached by investigators is an example:

> Deep-well injection systems for nearly all types of nonhazardous and hazardous industrial waste are a safe method of handling the waste if the systems are properly located, designed, operated, managed and regulated. Tentatively excluded as being safe for deep-well injection if containment is questionable are 13 chemicals and their related compounds indentified in the Assessment section.

But the following conclusions seem to contradict this:

> Weaknesses appear in limited areas in chemistry, microbiology, engineering, and geology in relation to deep-well injection.
>
> ...
>
> The effects of escaping wastes, or products of waste degradation on ground-water quality and aquatic life in surface water is essentially unknown.
>
> ...
>
> Reactions between waste, formation water, and formation minerals and the persistence period of compounds under varying conditions is not well understood. A better understanding of these reactions is essential if a good assessment of the overall effect of deep-well injection can be made.

If one strictly follows the guidelines established for this study, the stated shortcomings of deep-well injection would preclude assessing the technology as environmentally acceptable for many hazardous wastes. Again, however, one should consider that the definition of "environmentally acceptable" is not clear. It is a relative matter and will remain so until some absolute criteria are established.

There appears to be no black or white answer. Problems that have developed with deep-well systems can usually be traced to failure of making proper use of available geologic information, ignoring such information, or failure to follow proven engineering design and well-completion practices.

Implementation of proper practices appear to provide a degree of assurance that the injected waste will not harm the environment. Documents such as An Introduction to the Technology of Subsurface Wastewater Injection will aid this situation.

Even so, there are many who insist that, after a waste stream is injected underground, there is practically no control over what happens to it or where it goes.[5]

EPA's policy vis-a-vis subsurface injection is provided in the Federal Register, August 31, 1976. In summary, this policy is designed to meet three goals: (1) To protect the subsurface from pollution caused by improper injection or from improperly located wells; (2) to ensure that engineering and geological safeguards are adequate during all phases of subsurface injection operations, including preliminary investigations, design, construction, operation, monitoring and abandonment; and (3) to encourage development and use of better alternatives. EPA opposes waste injection without strict controls. The method should be used only if all other reasonable waste disposal alternatives have been explored and found unacceptable. EPA recognizes subsurface injection only as a temporary means of disposal, and as new technology becomes available, a change to more environmentally acceptable methods will be required.

SUMMARY STATEMENT

This paper presents only summary information contained in two voluminous reports dealing with subsurface injection of waste. One report[3] deals specifically with hazardous wastes and attempts to assess the technology's ability to dispose of hazardous wastes without adverse effects to the environment. The other report[4] provides details on the proper application of the technology and represents an extremely useful addition to the literature. Interested persons should refer to the full reports for details.

REFERENCES

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3. Reeder, L. R., J. H. Cobbs, J. W. Fields, Jr., W. D. Finley, S. C. Vokurka, and B. N. Rolfe. Review and Assessment of Deep-Well Injection of Hazardous Waste. EPA-600/2-77-029a. June 1977.

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DEVELOPING PRACTICAL METHODS FOR CONTROLLING EXCESS PESTICIDES

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ABSTRACT

Many hazardous materials are manufactured for specific industrial and agricultural applications. These materials often are applied for beneficial uses, and are accidentally spilled, or released through waste streams into the environment.

To reduce the impact of toxic and hazardous materials (whether in liquid, semi-liquid, or solid form) on the environment, several techniques have been developed and new promising technologies are continuously being developed. Ongoing research directed to determining if specially designed disposal pits can be used in an environmentally acceptable manner to control unwanted pesticides will be discussed.

INTRODUCTION

Promising technologies are continuously being developed to reduce the impact of toxic and hazardous materials (whether liquid, semi-liquid, or solid) on the environment. Although in the past excess materials have been disposed of by the quickest, easiest, and most economical means available, a recent increase in the supply of agricultural chemicals and, more importantly, an increase in concern for the environment places new emphasis on treatments needed prior to disposal.

Specialized techniques investigated by the U.S. Environmental Protection Agency (USEPA) for detoxification of toxic and hazardous materials include wet oxidation, chlorinolysis, sulfonation, catalysis, incineration, microwave plasma, encapsulation, and experimental disposal pits that prevent the loss of unwanted material while allowing biodegradation. The last, a promising technique for treatment of pesticides used by farmers and agricultural and commercial applicators, is discussed in this paper.

PIT DISPOSAL OF EXCESS HAZARDOUS MATERIALS

Ongoing work at Iowa State University includes development of a simple technique for the disposal of pesticides left unused in ground or aerial application operations. At present the safety and effectiveness of the various disposal systems in use by applicators have not been documented to the extent that USEPA can recommend this technique over others.

Since 1967, Iowa State Univeristy has developed and used a simple plastic-lined disposal pit at the Agronomy and Agricultural Engineering Research Station near Ames. In 1973, a more sophisticated concrete-lined pit was constructed at the Horticultural Research Station.

There has been no monitoring of either pit for effective degradation, possible loss by volatilization, or possible concentration of hazardous pesticides. To obtain adequate data on the disposal pits, a USEPA grant was awarded October 1975 to Iowa State University--specifically, to evaluate the effectiveness of pits currently in use and to determine the factors and parameters for improving the technique.

Some of the pesticides used at the Horticulture Station and deposited in the specialized pit are shown in Table I.

TABLE I

CHEMICALS USED AT HORTICULTURE STATION

Small amounts of leftover diluted materials were deposited.

Insecticides

Carbaryl 50%(sevin)
Chlordane 50%
Kelthane 35%
Pyrethrum 20%
Cythion 25% W.P.
Toxophene E.L.(6 lb/gal)
Guthion 50% W.P.
Lannate 90%
Heptachlor 30.2% + Xylene 44%

Herbicides

Dacthal
2,4-D
Paraquat
Amiben 23% W.P.
Tenoran 50% W.P.
Casoron

Fungicides

Benlate
Bravo 6F 54%
Captan
Maneb
Zineb
Sulfur

The chemical and microbiological studies, although incomplete, have revealed that many of the pesticides disposed in the pits can still be detected. Chemical analyses show pesticide concentrations in ppm for the horticultural farm disposal pit as sampled in March and June 1977.

After approximately a 1-year study of the pit, the major finding is that there has been no buildup of pesticide residues. This conclusion was substantiated by chemical and microbiological data. It is of interest to note that microbial numbers were similiar to what would be expected in a pit of this type, whether or not pesticides were present. The flora, however, were less diverse than would be expected in an open pit. Another predictable finding was that the pesticides in the pit were segregated. Samples taken from seven locations in the pit established that inhomogeneity existed.

As would be expected, a wide range of analytical results were obtained. These results were due in part to adsorption of pesticides to particles of soil. For this reason, the data could not be used to accurately calculate the total amount of pesticides discharged in the pit. The data were used, however, to establish trends and fate of the discharged pesticides.

The microbial flora identified in the pit consisted almost entirely of aerobic and facultatively aerobic bacteria; molds and yeast were present in low numbers and no strict anaerobes were detected. If a correlation with pesticide concentration and bacterial count existed, it was a trend toward higher counts in the areas containing greater pesticide concentrations.

OZONE TREATMENT

In an attempt to accelerate the pesticide degradation rates, a study was initiated to investigate ozone treatment of pesticides. In a review of the literature, several references to ozonation were found and used to establish experimental protocol.

In laboratory studies on ozonation, an ozone generator in the Engineering Department of Iowa State University was used. The necessary experimental apparatus for ozonation of pesticide solutions was procured and attached to this equipment. Operational conditions were established for the convenient determination of the possible reaction of selected pesticides with ozone. Ozonations were conducted for two hours at pH 5 and 13.5 for each of the test pesticides. The procedures allowed different solvent systems but 1:1 acetone/H_2O was used for most of the tests. Pesticide concentrations normally employed were 10^{-2}g/ℓ in 2ℓ solution volumes. Visual observations of color changes and precipitate formation, and chemical analyses for the depletion of the pesticide were used to determine which ozonations were successful.

Visual observations generally provided a convenient means of determining whether ozonation had any effect on the degradation of selected pesticides. With some additional work, a very rapid and useful screening procedure could be developed. For our preliminary study of ozonation as an aid to degradation the procedure as now used is satisfactory.

OZONATION OF SELECTED PESTICIDES

In this preliminary work eight chemicals were individually ozonated; aldrin, propachlor, alachlor, parathion, atrazine, treflan, endosulfan I and dimethylaniline. The results of these tests are summarized in Table II where the reaction results were determined by chemical analysis before and after ozonation at the listed pH values.

Atrazine, alachlor and treflan were also ozonated at higher concentrations in ethanol and these solutions were investigated to determine any improvements in degradation rates.

TEST THE BACTERIOLOGICAL ACTIVITY AFTER OZONATION OF SELECTED PESTICIDES

Bacteriological sampling of the pesticide dispsoal pit containing alachlor and atrazine yielded pure cultures of one alachlor degrader and three atrazine degraders. All the isolates proved to be gram negative, rod-shaped bacteria except one of the atrazine isolates that is a yeast. Each isolate is able to grow on the pesticide as its sole source of carbon and energy.

Quantitative growth studies in liquid media showed that the alachlor isolate grew exceptionally well in shake flasks, but the three atrazine isolates grew as well in stationary cultures as in shake flasks.

The three atrazine isolates are being used to examine the effect of ozonation upon atrazine degradation. Quantitative growth studies in broth to compare the rates of growth and the quantity of growth or ozone-treated and untreated atrazine are in progress. A preliminary qualitative growth study suggested that ozonation of atrazine may produce substances that inhibit the growth of the three isolates. The organic quantitative study should clarify this point for atrazine and other treated pesticides.

MINIPIT STUDY

In order to determine the degree of chemical alteration of pesticides in the horticultural disposal pit, a minipit experiment is being conducted as part of the larger project by personnel from the Departments of Agricultural Engineering, Agronomy, Bacteriology, Botany and Plant Pathology, Energy and Mineral Resource Research Institute, and Entomology at Iowa State University.

The minipit experiment consists of fifty-six (56) thirty (30) gallon polyethylene garbage cans partially buried in the ground and arranged in seven 8-can rows or a 7 x 8 grid. Four rows contain herbicides (alachlor, atrazine, 2,4-D, and trifluralin), with one herbicide per row in different amounts and concentrations. Two rows contain insecticides (carbaryl and parathion), one per row, again in different amounts and concentrations. The last row contains mixtures of all six pesticides. The eight garbage cans per row alternately contain 300 gram, 0.5% (w/w) and 15 gram, 0.025% (w/w) pesticide samples. The 0.5% (w/w) concentration represents a reasonable, practical application concentration. The 0.025% (w/w) concentration approxi-

TABLE II

RESULTS OF OZONATION TESTS

Compound	Reaction at		Products
	pH=5	pH=13.0	
aldrin	positive	not tested	dieldrin, unknowns
propachlor	negative	negative	
alachlor	negative	slight	
parathion	negative*	negative*	
endosulfan I	negative	positive	unknown
treflan	slight	positive	unknown
dimethylaniline	some	positive	unknown
atrazine	some	positive	unknown

*heterogeneous reaction mixture probably responsible for negative results here.

mates the dilution one might obtain by rinsing the tank on equipment used to apply the pesticide.

Half of the cans contain 0.1% (w/v) peptone as a nutrient. The contents of half the cans (some with, some without nutrients) are aerated using a small compressor, a polyvinyl chloride manifold, and tygon tubing leading to each fritted glass aerator. The entire area is protected by a wire fence and warning signs. Garbage can lids are kept in place between sampling periods.

Analyses and evaluations for both the minipits and large pit will be completed by November 1978. It is expected that the results will show whether a low-cost, improved pit disposal system can be developed and recommended for wide-scale use in the disposal of unwanted pesticides.

SUMMARY

The pesticide disposal pit (macro) located at Iowa State University's horticulture station has been in use for seven years. Water and soil samples were analyzed during the 1976-77 growing season for chemical, biological and microbial activity and content. The major finding, as substantiated by chemical and microbiological data, is that no build-up of pesticide residues in the pit occurs. Sampling and analyzing of the pit at various locations revealed that inhomogeneity of pesticide distribution existed. Consequently, minipit experiments were designed to determine trends in pesticide degradation, and the overall fate of pesticides disposed of in the pits.

It is expected that at the conclusion of 1978, sufficient data will be available for full-scale demonstration of this disposal technique.

REFERENCE

1. U.S. Environmental Protection Agency Grant No. R804533-02, "Development of Safe Disposal Methods for Disposal of Excess Pesticides Used by Farmers and Agriculatural Applicators." (Awarded October 1975 to Present.)

Attendance List

Fourth Annual Research Symposium

Land Disposal of Hazardous Waste
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